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CHEMICAL TECHNOLOGY AND ANALYSIS

OF

OILS, FATS, AND WAXES

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CHEMICAL TECHNOLOGY AND ANALYSIS

OF

OILS FATS AND WAXES

BY

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CHAPTER XV

TECHNOLOGY OF MANUFACTURED OILS, FATS, AND WAXES—TECHNICAL AND COMMERCIAL EXAMINATION OF THE PRODUCTS OF THE OIL, FAT, AND WAX INDUSTRIES.

I. Technology of Oils and Fats[1]

SYNTHETICAL FATS

The " biochemical " synthesis of oils and fats, although carried out by nature on an enormous scale, with the aid of water, from the lowest carbon derivatives, such as carbon dioxide, aldehyde, etc., does not yet fall within the purview of manufacturing operations. Since the supply of natural oils and fats is wellnigh inexhaustible, their technical preparation by synthetical methods has no practical importance, except in the case of *acetin*, the triglyceride of acetic acid (see below).

The synthetical methods for preparing triglycerides—including those for mono- and di-glycerides—have been described in Chapter I. As the raw materials used in all synthetical methods are the proximate constituents which glycerides yield on hydrolysis, strictly speaking these methods cannot be termed synthetical ones, as the starting material is actually the product which it is desired ultimately to obtain. Hence all these syntheses, important though they may be when working on a laboratory scale, do not deserve further attention from a technological point of view, although they may find an use on a large scale in converting the free fatty acids in an oil or fat into neutral glycerides. For this purpose are employed such methods as heating with glycerin to 220° C. under reduced pressure,[2] the action of the *Twitchell* reagent on a mixture of fatty acids and glycerin,[3] or the action of enzymes. Greater interest would attach to them if it were possible to prepare on a commercial scale fatty acids synthetically from a different raw material such as the hydrocarbons which are found in abundant quantities in natural petroleum. The problem would then resolve itself into converting a CH_3 group of hydrocarbons, of a boiling point in the neighbourhood of 300° C., into the carboxyl group. The introduction of halogen into aliphatic hydrocarbons has been patented.[1] Acid bodies have been prepared by *M. Bergmann*[2] by blowing air through paraffin wax at a temperature of 135° C. The final product was a brown oily mass having an acid value of 132. Lignoceric acid was identified among its constituents. Inasmuch as the time required for the operation was fifteen to eighteen days, the process can hardly be described as commercially practicable.

---

[1] Cp. Lewkowitsch, " Problems in the Fat Industry," *Journ. Soc. Chem. Ind.*, 1903, 592.

[2] Bellucci, *Gaz. chim. ital.*, 1912, ii. 283. Cp. also Bellucci and Manzetti, *Atti R. Accad. d. Lincei*, 1911, i. 125; Gianoli, *Soc. chim. ital.*, April 1911.

[3] Krause, *Journ. Soc. Chem. Ind.*, 1911, 633; Iwanow, *Berichte d. Deutsch. Botan. Ges.* 1911, 595.

C. Kelher[3] obtained by oxidising paraffin wax a compound having an iodine value of 1-2. Its saponification value was 250-300, and from it he isolated capric, myristic, palmitic, heptadecoic, stearic and arachidic acids. It also contained an acid having the formula $C_{16}H_{32}O_2$ previously identified by *Burgoyne* and which he described as isopalmitic acid. Some promising attempts seem to have been made by the application of *Grignard's* reaction (conversion of hydrocarbons by means of metallic magnesium into metallo-organic compounds and subsequent treatment of the latter with carbonic acid).[4] For a consideration of the action of *Grignard's* reagent on esters and dibasic acids cp. *Hewitt and Steinberg*.[5] *Zelinsky*[6] has indeed succeeded in synthesising acids containing up to ten atoms of carbon in the molecule, and in preparing a di- and a tri-octin from an acid of the formula $C_8H_{14}O_2$, by heating it with glycerol to 250° C. It, however, should be remembered that acids with more than ten atoms of carbon show an essentially different behaviour in chemical reactions from that of the lower fatty acids.

Attempts have also been made to convert the petroleum hydrocarbons into alcohols which on treatment with soda lime would yield fatty acids.[7] By the oxidation of petroleums by *Etard's* method[8] and subsequent treatment of the product of reaction with sodium bisulphite solution, *Schulz*[9] obtained only about 5 per cent of bodies which combine with the bisulphite. On oxidation with nitric acid these bodies yielded non-crystallisable compounds having an acid reaction. *Liebermann and Zsuffa*[10] attempt to convert aromatic hydrocarbons into carboxylic acids by the action of oxal chloride.

The preparation of glycerides from acids derived from hydrocarbons by *Grignard's* reaction must not be confounded with the production of glycerides from naphthenic acids, for these acids are found as such ready formed in petroleum. Moreover, the glycerides obtained from naphthenic acids exhibit a totally different behaviour from that of the naturally formed glycerides, the most characteristic difference being that they are heavier than water, having the specific gravity of 1·008 at 15° C. The use of naphthenic acids and their glycerides for the preparation of india-rubber substitutes and plastic masses has been patented by *Chercheffsky*.[1] The acids themselves also differ totally from the ordinary fatty acids containing the same number of carbon atoms in the molecule. Since it is extremely probable that natural oils and fats are built up from carbohydrates (cp. Vol. I. 1), attempts have been made to prepare synthetic fats from glucose by the aldol reaction.[2]

---

[1] Badische Anilin u. Soda Fabrik, English patent 5126, 1912 ; Pfeifer and Szarvasy, United States patent 1,012,149 ; Orechoff and Konowaloff, *Berichte*, 1912, 861.

[2] *Journ. Soc. Chem. Ind.*, 1918, 362 A.

[3] *Berichte*, 1920, 53, 1567.

[4] Cp. Simonis and Kirschten, *Berichte*, 1912, 568 ; Hibbert, *Proc. Chem. Soc.*, 1912, 15 ; Zarewitinoff, *Berichte*, 1912, 2384.

[5] *Proc. Chem. Soc.*, 1912, 140.

[6] *Berichte*, 1902, 2687. Cp. also *Journ. Russ. Phys. Chem. Ges.*, 1909 ; *Chem. Zeit. Rep.*, 1909, 631.

[7] Bjelouss, *Berichte*, 1912, 627,

[8] *Ann. Chim. Phys.*, 1881, 218.

[9] *Petroleum*, 1910, 189.

[10] *Berichte*, 1911 208. Cp. also Standinger, *Berichte*, 1908, 3558, 1909, 3485, 3966 ; Ullmann, French patent 418,088.

Bellucci states that by heating cetyl alcohol with stearic acid in equimolecular portions at 220° C. in a current of carbon dioxide for two hours, 95 per cent of the theoretical yield of cetyl stearate is obtained.[3]

Acetine

Acetine is used as a solvent (possessing certain advantages over other solvents, such as alcohol, etc.) for indulin and other colouring matters employed by the calico printer as steam colours.

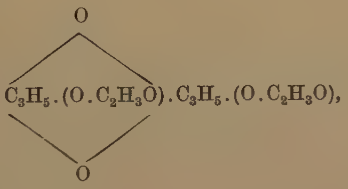
More recently it has been employed as an adulterant of peppermint oil and other ethereal oils, and for gelatinising acetyl cellulose.

Commercial "acetine" is prepared by heating together glycerin and glacial acetic acid (Vol. I. Chap. I.).

As *Geitel*[4] has shown, there are always formed simultaneously triacetin, diacetin, and monoacetin in varying quantities, depending on the special condition of each experiment, whilst a certain amount of glycerol remains unchanged. Furthermore, the several acetins react with glycerol to form products of condensation, such as monoacetyldiglycerol.

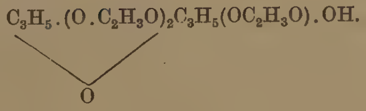
$$C_3H_5.(OH)_2-O-C_3H_5.(O.C_2H_3O).OH,$$

and diacetyldiglycid



$$C_3H_5.(O.C_2H_3O).C_3H_5.(O.C_2H_3O),$$

and triacetyldiglycerol



$$C_3H_5.(O.C_2H_3O)_2C_3H_5(OC_2H_3O).OH.$$

---

[1] German patent 228,858.

[2] Cp. Perkin, *Journ. Soc. Chem. Ind.*, 1912, 623; cp. also Franke and Wozelka, *Monatsh. f. Chem.*, 1912, 349; Buchner and Meisenheimer, *Berichte*, 1908, 1410.

[3] *Chem. Zeit.*, 1911, 669.

[4] *Journ. f. prakt. Chem.*, 1897 (55), 428.

For purposes of practical analysis, however, it may be assumed that commercial acetine consists of a mixture of diacetin and triacetin. Besides these, the commercial preparations contain free acetic acid and water.

The proportions of diacetin and triacetin are found by estimating, on the one hand, the combined acetic acid, and, on the other hand, the glycerol by the acetin process (Vol. I. Chap. VI.). The analysis is carried out as follows :—

An accurately weighed quantity of the sample is neutralised with half-normal aqueous potash, using phenolphthalein as an indicator. Thus the *free acetic acid* is obtained. Then run into the neutralised solution a measured quantity of caustic soda of 1·1 specific gravity, the strength of which is ascertained by titrating with half-normal hydrochloric acid, and boil for half an hour, whereby the diacetin and triacetin are saponified, the liberated acetic acid combining with the caustic soda. After titrating back the excess of caustic soda with half-normal hydrochloric acid, the number of c.c. of half-normal caustic soda used for 1 grm. of substance is found.

A fresh quantity—about 1·5 to 2 grms.—of the sample is then weighed off accurately and the glycerol determined as described (Vol. I. Chap. VI.). The proportion of water is found by difference.

Suppose 1 grm. of the sample required 2 c.c. of half-normal caustic soda for neutralisation, then the sample contains $\frac{2 \times 6}{2}$[1] $= 6$ per cent of *free acetic acid.* Let the number of c.c. of half-normal caustic soda required to neutralise the acetic acid formed on saponifying (*combined acetic acid*) in *one* gram be 20 c.c., and the percentage of glycerol found be 33·3 per cent. It is convenient to calculate the *combined* acetic acid to C_2H_2O (42), as the sum of the percentages of C_2H_2O and of glycerol equals the sum of the diacetin and triacetin in the sample. The proportion of combined C_2H_2O is $20 \times 2{\cdot}1 = 42$ per cent. Let x and y be the percentages of diacetin and triacetin respectively, then we have

$$x + y = 42 + 33{\cdot}3 = 75{\cdot}3 \quad . \quad . \quad . \quad . \quad (1).$$

One molecule of diacetin, or 176 parts, yields 92 parts of glycerol; one molecule of triacetin, or 218 parts, also yields 92 parts of glycerol, hence

$$\frac{92x}{176} + \frac{92y}{218} = 33{\cdot}3 \quad . \quad . \quad . \quad . \quad . \quad (2).$$

From equations (1) and (2) we find $x = 15{\cdot}18$ and $y = 60{\cdot}12$. The sample has, therefore, the following composition :—

Triacetin	60·12 per cent.
Diacetin	15·18 ,, ,,
Acetic acid	6·00 ,, ,,
Water (by difference)	18·70 ,, ,,
	100·00

---

[1] Acetic acid $C_2H_4O_2 = 60$.

EXTENT OF OIL AND FAT INDUSTRIES

The raw materials of the oil and fat industries are furnished by the oils and fats, which have been described in the preceding chapter. The extent and importance of the industries with which we shall deal in this chapter and the next may be gathered from the following statistical data; those referring to the trade of this country may be considered as being fairly complete :—

TABLE I.—IMPORTS

	1898–1900.	1901–3.	1904–6.	1907–9.	1910.	1911.	1912.
	£	£	£	£	£	£	£
Butter	50,625,734	60,622,793	66,163,984	44,842,888	24,493,450	24,600,619	25,354,193
Margarine	7,398,682	7,439,800	7,963,998	6,548,627	2,935,244	2,461,325	3,514,045
Cacao Butter	138,182	56,988	60,940	142,034	33,917	96,448	58,007
Oleomargarine	821,283	951,798	1,410,385	3,324,427	1,116,383	739,974	834,282
Lard	9,223,358	12,027,455	11,396,361	13,756,975	4,520,074	4,251,758	4,573,136
Imitation Lard	277,664	745,702	866,257	1,153,801	603,444	360,878	434,623
Oils—							
Fish, Train, Blubber, Sperm, or Head Matter	1,086,056	1,355,575	1,319,345	1,767,209	927,231	1,252,663	1,296,477
Animal	254,366	409,712	629,315	648,836	146,654	243,420	280,693
Castor	407,509	426,756	203,534	170,635	39,334	57,398	40,122
Coconut—	1,556,954	2,308,187	2,670,654	Subdivided	since 1904	...	...
Unrefined	...	...	...	2,144,420	1,013,629	1,001,227	1,202,527
Refined	...	...	...	862,546	1,136,736	1,259,083	1,327,955
Olive	1,622,492	1,735,760	1,493,829	Subdivided	since 1904	...	...
Unrefined	...	...	...	772,656	299,922	200,619	386,239
Refined	...	...	...	831,685	386,189	296,824	402,894
Palm	3,089,247	4,476,375	4,394,286	Subdivided	since 1904	...	...
Unrefined	...	...	...	5,691,019	3,056,614	2,474,320	2,375,530
Refined	...	...	...	167,271	111,800	223,777	90,335
Seed Oils	2,607,669	2,959,553	Subdivided	...	...	...	...
Cotton Seed Oil	...	...	785,254	Subdivided	...	...	...
Unrefined	...	...	...	92,358	22,984	98,129	168,852
Refined	...	...	...	1,249,157	562,672	713,925	660,268
Linseed Oil	...	...	592,877	Subdivided	...	...	...
Pure	...	...	...	939,009	1,252,141	1,170,165	1,128,224
Not Pure	...	...	...	73,385	25,477	9,527	3,747
Rape Seed Oil	...	...	783,227	854,250	359,166	246,193	252,626
Other sorts	...	...	418,613	609,216	398,597	440,334	555,679

Seeds—							
Cotton	6,730,111	8,975,343	9,127,586	13,184,199	4,865,836	4,398,675	4,800,116
Linseed	10,466,752	12,930,555	11,318,385	12,466,452	4,495,718	4,728,536	4,366,199
Rape	921,409	1,101,405	907,137	1,080,963	443,530	431,376	376,939
Soya Beans	...	...	...	1,921,750	953,884	1,648,195	1,567,960
Other Seeds	1,082,099	1,474,889	1,853,882	5,037,713	923,549	564,250	379,188
Tallow and Stearine	7,281,683	7,029,855	7,413,652	9,976,548	4,194,489	3,671,248	3,580,104
Candles	72,744	80,604	86,622	44,470	14,497	16,694	13,549
Oil Cake—							
Linseed	4,951,548	3,665,178	3,490,431	2,929,653	860,015	428,042	491,375
Cotton Seed	2,804,772	3,085,066	2,809,678	2,886,727	953,884	1,128,598	1,715,936
Rape Seed	...	...	108,337	170,272	111,034	212,704	85,889
Other sorts	224,809	301,760	289,007	497,008	185,671	194,300	205,621
Soap (transparent)	1,889	1,400	1,121	1,353	556	791	937
Soap and Soap Powder	244,345	860,799	3,220,087	Subdivided	...	...	...
Soap Powder	...	...	...	136,426	40,154	43,409	45,727
Soap Stock	...	...	...	131,247	13,535	28,679	61,789
Soap, Household	...	284,401	848,566	774,965	225,358	212,688	186,879
Toilet	...	97,696	280,169	283,383	99,429	94,317	104,757
Soft Soap	...	...	...	3,303	2,328	3,879	3,840
Polishing and Scouring Soaps	...	...	...	2,955	1,764	4,754	6,559
Other sorts	...	...	...	287,947	70,904	84,689	113,814
Linoleum, Oil, and Floorcloth	199,661	227,997	301,908	Subdivided	...	...	...
For Floors	...	...	...	221,507	65,020	74,360	69,730
For Furniture	...	...	...	28,697	6,585	16,399	17,119
For other purposes	...	...	...	886	142	76	296
Varnish	149,053	155,875	179,436	178,823	68,183	70,894	74,740
Glycerine	...	128,915	343,827	347,906	Subdivided	...	...
Crude	...	...	...	...	179,970	308,998	303,066
Distilled	...	...	...	...	49,990	75,260	91,421
Rosin	...	482,209	2,185,691	2,333,031	880,582	1,089,685	1,248,524
Nuts and Kernels for expressing for Oil	...	828,690	2,454,770	3,358,313	1,915,279	1,622,955	1,750,777
Blacking and Polishes	...	167,669	479,426	448,356	146,241	138,678	49,804
Cattle Foods—							
Sweetened	...	4,572	150,825	235,689	105,206	99,411	113,539
Other sorts, not Oil Cake	...	...	158,917	360,500	129,998	131,733	190.411
Paraffin Wax	...	1,079,405	3,295,636	3,430,857	1,017,014	815,838	1,182,380

TABLE I.—IMPORTS—*continued*

	1913.	1914.	1915.	1916.	1917.	1918.	1919.	1920.
	£	£	£	£	£	£	£	£
Butter	24,083,658	24,014,276	27,022,745	18,964,002	18,895,707	19,769,738	19,854,427	24,518,748
Margarine	3,917,701	3,977,361	5,751,253	8,983,007	7,778,285	1,563,405	2,229,838	5,514,325
Cacao Butter	122,159	204,069	89,244	169,600	12,676	30,218	330,195	211,138
Oleomargarine	858,130	793,533	1,628,557	2,086,489	2,940,209	7,745,735	6,236,596	3,754,017
Lard	5,552,462	4,750,943	5,783,260	6,982,985	8,942,355	21,063,529	18,673,125	12,793,129
Imitation Lard	465,503	525,185	444,723	470,904	244,359	185,037	796,839	223,829
Oils—								
Fish, Train, Blubber, Sperm, or Head Matter	1,508,416	1,139,400	2,278,065	3,493,474	2,279,142	4,050,311	3,784,162	3,519,574
Animal	298,026	262,969	271,915	120,270	101,406	320,499	799,729	249,062
Castor	41,875	25,542	28,261	249,125	219,373	422,574	29,186	39,140
Coconut—								
Unrefined	1,342,469	807,463	1,408,286	1,087,313	1,310,230	4,060,296	4,354,319	5,804,393
Refined	1,316,246	739,902	844,596	464,723	106,459	31,203	2,537,139	353,566
Olive—								
Unrefined	130,191	266,563	224,827	272,272	168,081	244,065	266,782	261,908
Refined	385,257	396,849	382,763	344,307	205,348	602,200	734,836	546,460
Palm—								
Unrefined	2,326,842	2,257,645	1,953,427	2,198,984	3,209,004	3,935,487	6,441,257	6,982,627
Refined	141,967	138,364	1,232	...	75	...	307,531	37,914
Seed Oils—								
Cotton Seed Oil—								
Unrefined	31,748	89,851	106,504	28,574	9,363	119,228	250,978	198,639
Refined	558,277	659,475	1,115,973	516,227	739,841	1,902,995	2,706,098	711,687
Linseed Oil—								
Pure	310,157	129,190	6,615	160	4,302	5,931	101,866	...
Not Pure	513	2,442	...	75	220	...	3,290	...
Rape Seed Oil	222,556	198,162	250,443	307,233	120,585	13,145	387,699	146,982
Other sorts	767,810	808,001	1,302,831	1,884,805	618,929	225,641	758,628	304,663

Seeds—								
Cotton	4,648,617	4,420,307	4,122,493	4,448,933	4,002,107	6,469,762	9,773,600	8,453,765
Linseed	7,195,399	5,723,846	5,573,622	9,356,631	5,438,130	8,158,170	20,662,835	15,688,378
Rape	531,725	622,927	464,229	1,271,489	1,480,745	1,662,008	2,707,832	1,090,060
Soya Beans	635,747	503,190	1,428,281	960,356	499,813	...	1,640,639	350,923
Other Seeds	233,240	336,381	912,053	991,348	234,943	216,528	436,056	523,411
Tallow and Stearine	3,375,072	2,852,676	3,111,465	2,302,584	1,979,274	1,697,902	7,887,202	4,059,262
Candles	16,929	17,713	20,755	34,983	12,521	2,595	56,522	95,728
Oil Cake—								
Linseed	626,118	360,508	651,815	937,312	1,483,833	164,411	1,639,245	954,013
Cotton Seed	1,407,023	1,083,478	1,614,462	2,017,790	2,092,801	45,623	4,012,597	1,629,032
Rape Seed	156,592	184,092	47,623	7,141	9,216	...	4,000	138,166
Other Seeds	350,159	360,761	959,259	153,704	52,294	...	164,688	487,426
Soap (transparent)	1,074	715	387	91	...	...	...	...
Soap and Soap Powder	...	...	...	...	...	...	...	...
Soap Powder	52,900	48,210	54,845	23,673	60	112	9,673	...
Soap Stock	41,487	58,612	20,752	5,546	2,060	1,199	119,998	66,922
Soap, Household	195,454	130,658	226,614	114,342	9,795	1,494	304,580	179,458
Toilet	130,052	111,664	140,594	88,178	12,078	24,334	199,722	75,333
Soft Soap	5,253	5,972	3,565	1,181	...	197	...	...
Polishing and Scouring Soap	5,667	4,862	4,343	2,651	...	...	15,715	...
Other Sorts	91,963	109,994	122,858	124,110	43	...	303,799	8,431
Linoleum, Oil, and Floorcloth—								
For Floors	86,653	49,585	12,624	5,395	...	...	21,226	...
For Furniture	29,680	24,603	24,336	11,699	690	...	29,477	286,902
For other purposes	769	679	776	533	...	...	6,248	39,503
Varnish	67,219	52,419	36,061	37,468	16,153	469	47,699	85,954
Glycerine—								
Crude	255,718	258,200	272,029	101,007	43,518	490,343	363,933	111,435
Distilled	84,570	65,769	165,862	104,144	128,824	376,937	10,729	56,029
Rosin	1,120,652	822,093	1,200,483	1,888,887	2,466,134	1,808,608	3,819,122	2,798,548
Nuts and Kernels for expressing for Oil	1,933,052	3,595,417	8,030,456	8,532,032	12,616,637	12,696,553	17,192,729	18,007,311
Blacking and Polishes	53,942	42,954	33,450	78,245	81,206	47,966	124,180	95,687
Cattle Foods—								
Sweetened	98,852	63,451	64,163	20,036	37,841	46,073	34,180	129,299
Other sorts, not Oil Cake	189,588	153,155	282,590	880,314	385,944	32,764	1,624,745	235,296
Paraffin Wax	983,989	862,368	1,531,816	2,054,463	2,506,816	3,343,187	2,977,102	4,244,014

TABLE II.—EXPORTS

	1898–1900.	1901–3.	1904–6.	1907–9.	1910.	1911.	1912.
	£	£	£	£	£	£	£
Butter	168,718	201,847	168,966	182,722	56,256	70,631	72,029
Margarine and all artificial Butters	31,131	39,141	105,780	231,101	176,930	93,570	78,731
Oleomargarine	65,631	58,188	35,772	137,880	206,360	351,496	437,873
Lard	...	...	24,049	67,358	21,142	30,429	30,818
Imitation Lard	...	...	622	3,573	6,616	8,255	6,358
Oils—							
Coconut—							
Unrefined	...	...	105,695	264,054	126,710	72,794	142,978
Refined	..	...	30,445	296,517	430,663	126,750	109,179
Olive—							
Unrefined	...	...	1,259	4,798	1,354	601	912
Refined	...	...	8,551	117,856	49,125	41,982	44,052
Palm—							
Unrefined	...	...	11,859[1]	15,363[1]	84,801[1]	53,022[1]	21,315[1]
Refined	...	...	25,349[1]	63,251[1]	23,548[1]	14,518[1]	21,359[1]
Seed Oils—							
Cotton Seed Oil	969,485	1,553,250	1,268,004	Subdivided	since 1904	...	...
Unrefined	...	...	...	100,688	11,979	9,317	14,962
Refined	...	...	...	1,897,644	874,571	661,639	533,799
Linseed Oil	1,442,283	1,880,246	1,763,976	Subdivided	since 1904	...	...
Pure	...	...	...	1,626,958	837,712	1,050,856	895,318
Not pure	...	...	...	171,184	98,851	120,838	123,294
Rape Seed Oil	...	...	241,395	439,903	141,368	187,140	170,269
Soya Bean Oil	...	...	...	...	...	630,073	504,668
Other Seed Oils	230,316	336,360	96,362	421,767	1,122,146	52,578	163,496

[1] Including palm kernel oil.

Grease, Tallow, and Animal Fats	2,368,971	2,487,372	2,430,550	2,928,483	965,688	730,792	669,037
Candles [1]	1,139,486	1,393,931	1,782,269	1,550,979	485,218	417,609	425,735
Oil Cake	200,336	513,159	Subdivided	since 1903	...	...	...
Linseed	...	...	7,617	5,178	5,021	24,729	50,391
Cotton Seed	...	...	146,609	106,514	49,613	28,958	30,091
Rape Seed	...	...	31,209	14,987	...	1,603	1,709
Soya Bean Cake	...	...	...	...	...	592,176	334,750
Other sorts	...	...	172,609	253,311	1,032,549	73,062	131,707
Soap	2,710,695	2,125,626	Subdivided	since 1902	...	...	...
Soap Powder Soap Stock	...	26,126	85,546	85,288	30,790	33,906	35,204
Household	...	900,573	2,979,263	3,288,984	1,357,776	1,511,061	1,580,697
Toilet	...	217,956	738,185	884,255	357,781	383,184	404,701
Soft Soap	...	...	...	39,396	24,487	29,023	32,609
Polishing and Scouring Soaps	...	...	...	31,798	16,070	15,520	14,100
Other sorts, including Cotton Seed Oil Soap	...	...	...	30,816	10,639	9,889	6,213
Glycerine	...	326,419	910,876	1,200,582	...	...	...
Crude	...	...	...	...	338,565	326,747	322,728
Distilled	...	...	...	...	314,615	434,049	330,841
Blacking and Polishes	...	204,996	819,761	1,075,437	436,515	457,863	528,410
Cattle Foods—							
Sweetened	...	16,003	14,333	8,738	3,791	6,184	22,947
Other sorts, not Oil Cake	...	...	407,590	766,059	461,171	473,266	579,631
Oil and Floorcloth	3,477,547	1,540,101	5,493,966	...	...	...	...
For Floor	...	...	...	4,933,432	1,932,742	1,955,535	2,018,798
For Furniture	...	...	...	1,442,308	611,602	631,292	671,895
For other purposes	...	...	...	233,826	87,297	102,441	100,374
Paraffin Wax	...	247,113	966,175	1,085,515	288,457	252,519	267,463

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[1] Containing paraffin wax.

TABLE II.—EXPORTS—*continued*

	1913.	1914.	1915.	1916.	1917.	1918.	1919.	1920.
	£	£	£	£	£	£	£	£
Butter	65,065	64,934	76,347	72,308	23,660	23,037	33,433	53,887
Margarine and all artificial Butters	75,066	55,693	59,059	78,326	50,817	78,987	490,976	493,007
Oleomargarine	526,466	368,499	390,969	223,076	50,002	10,904	113,952	406,853
Lard	21,902	32,494	67,157	54,114	16,416	7,614	33,184	21,873
Imitation Lard	4,605	1,804	2,584	4,987	4,218	1,933	219,707	216,600
Oils—								
Coconut—								
Unrefined	127,465	105,709	78,783	29,539	50,961	38,349	89,412	61,534
Refined	141,777	147,631	266,773	125,140	39,832	100	44,312	228,457
Olive—								
Unrefined	1,183	626	625	444	...	...	252	9,326
Refined	45,487	36,552	32,158	33,932	16,751	427	21,257	83,823
Palm—								
Unrefined	43,096[1]	138,331[1]	334,919[1]	136,458[1]	60,414	10,030	26,611	90,834
Refined	24,169[1]	39,264[1]	103,190[1]	58,224[1]	53,512	2,800	42,097	110,597
Seed Oils—								
Cotton Seed Oil—								
Unrefined	15,453	13,198	127,208	6,327	81,290	...	449,471	539,961
Refined	755,083	864,037	677,909	101,197	38,961	2,989	279,870	1,179,264
Linseed Oil—								
Pure	794,150	639,986	1,673,876	971,806	912,309	51,719	6,952,027	3,035,837[2] 1,231,197[3] 692,370[4]
Not pure	86,683	48,389	55,109	56,115	124,769	56,838		
Rape Seed Oil	175,846	206,192	218,022	180,327	922,163	219,380	1,308,138	729,466
Soya Bean Oil	294,238	305,059	430,387	182,415	37,435	...	113,589	1,129,459
Other Seed Oils	61,240	89,853	105,908	70,476	454,784	342,779	133,595	63,890

[1] Including palm kernel oil. [2] Raw. [3] Boiled. [4] Refined.

Grease, Tallow, and Animal Fats	848,100	837,647	799,932	823,242	1,874,272	275,656	2,134,931	2,742,107
Candles [1]	434,983	375,784	488,831	669,652	536,176	107,849	1,260,631	1,232,127
Oil Cake	...	...	...	...	...	...	...	...
Linseed	47,094	31,981	1,063	804	834	825	5,278	50,194
Cotton Seed	36,638	17,265	19,609	142	284	444	703	94,425
Rape Seed	5,121	2,205	2,070	38	5	...	...	21,233
Soya Bean Cake	208,899	61,322	156,227	36,132	20	...	...	11,362
Other sorts	56,292	153,054	56,896	13,149	398	251	85,784	77,717
Soap—								
Soap Powder / Soap Stock	28,004	31,527	24,863	30,619	28,530	19,174	...	...
Household	1,598,452	1,696,383	1,905,008	2,670,616	4,057,129	3,299,179	7,091,263	5,624,637
Toilet	412,541	414,039	457,912	641,961	621,353	647,141	1,417,031	1,770,417
Soft Soap	31,435	25,765	98,037	90,416	135,939	70,216	267,319	123,911
Polishing and Scouring Soap	13,970	9,784	10,476	14,743	14,429	12,404	21,379	38,450
Other sorts, including Cotton Seed Oil Soap	8,284	8,776	10,651	10,253	10,975	16,902	110,720	110,506
Glycerine—								
Crude	442,635	153,369	423,526	153,565	109,066	61,886	36,486	727,342
Distilled	378,746	334,412	377,942	320,999	298,926	220,419	322,456	848,794
Blacking and Polishes	564,998	490,658	490,353	685,645	624,290	420,083	1,080,067	1,611,118
Cattle Foods—								
Sweetened	36,943	23,482	13,365	8,674	1,982	5	...	16,363
Other sorts, not Oil Cake	522,204	291,599	385,777	288,928	34,519	27,575	120,811	469,046
Oil and Floorcloth	...	...	...	...	...	...	...	...
For Floor	1,870,118	1,589,469	1,089,450	1,421,723	1,159,029	777,065	...[2]	...[2]
For Furniture	665,950	546,908	418,165	576,631	424,067	519,839	1,467,283	2,530,236
For other purposes	96,280	70,249	57,679	73,341	97,477	77,713	2,178,691	945,507
Paraffin Wax	320,011	254,506	327,836	410,969	521,745	72,799	557,715	751,439

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[1] Containing paraffin wax.

[2] Included in "For other purposes."

TABLE III.—RE-EXPORTS

	1898–1900.	1901–3.	1904–6.	1907–9.	1910.	1911.	1912.
	£	£	£	£	£	£	£
Butter	936,739	796,025	1,163,972	1,109,063	384,088	759,214	715,096
Margarine and all artificial Butters	85,992	110,466	64,572	50,448	17,420	23,488	16,474
Cacao Butter	6,713	2,009	800	4,676	2,239	986	386
Oleomargarine	197,320	225,086	474,441	855,486	467,008	306,743	455,821
Lard	1,966,428	896,951	1,015,159	1,267,535	353,907	504,984	580,021
Imitation Lard	18,483	9,203	14,157	13,253	10,815	12,416	7,676
Oils—							
Fish, Train, or Head Matter, Blubber, Sperm . . .	88,487	103,960	111,926	99,059	82,499	130,972	270,841
Animal	28,894	10,169	17,687	14,544	10,419	6,999	10,223
Castor	55,998	49,175	24,926	8,993	2,142	2,246	1,909
Coconut—	391,691	700,295	858,699	Subdivided	since 1904	...	...
Unrefined	...	...	...	656,442	229,203	124,109	134,723
Refined	...	...	...	53,424	20,464	22,321	38,513
Olive	360,611	362,461	294,430	Subdivided	since 1904	...	...
Unrefined	...	...	...	76,637	13,920	19,083	33,483
Refined	...	...	...	164,975	53,713	46,460	82,373
Palm	2,002,857	2,435,267	2,514,867	Subdivided	since 1904	...	...
Unrefined	...	...	...	3,249,126	1,820,598	1,330,040	1,310,981
Refined	...	...	...	2,323	...	78	1,468
Seed Oils	202,226	246,007	88,317	Subdivided	since 1903	...	...
Cotton Seed Oil	...	...	...	Subdivided	since 1904	...	...
Unrefined	...	...	...	6,016	1,316	914	37,874
Refined	...	...	...	143,173	39,315	28,888	34,879
Linseed Oil	...	...	12,728	Subdivided	since 1905	...	...
Pure	...	...	...	14,419	25,747	8,014	17,618
Not Pure	...	...	...	3,095	...	46	...
Rape Seed Oil	...	...	10,782	16,958	2,624	4,682	1,858
Other sorts	...	...	147,408	83,340	32,048	67,970	32,147

Seeds—							
Cotton	8,450	4,826	8,456	6,783	1,556	16,657	2,739
Linseed	755,214	971,433	466,268	364,200	527,707	273,098	68,434
Rape	137,947	113,905	37,140	32,193	7,417	5,008	6,872
Soya Bean	...	...	...	...	60,544	23,137	13,494
Castor	...	...	...	...	...	258,536	159,577
Other sorts	622,647	818,642	624,591	1,042,282	301,655	50,191	74,964
Tallow and Stearine	3,463,479	2,179,015	3,754,337	4,965,840	2,259,427	2,001,387	1,654,624
Candles	39,452	40,565	32,718	10,923	2,258	3,799	1,518
Oil Cake—							
Linseed	6,944	3,247	24,913	17,061	16,458	2,486	4,108
Cotton Seed	447	2,167	6,608	8,159	61	1,627	5,757
Rape Seed	...	...	1,008	290	...	...	...
Other sorts	72,339	66,544	27,526	29,952	11,315	4,433	4,144
Soap and Soap Powder	18,434	35,877	Subdivided	since 1902	...	...	...
Soap (transparent)	366	117	...	39	48	32	75
Soap Powder	...	1,527	5,382	704	137	295	127
Soap Stock				6,707	200	1,814	1,411
Soap, Household	...	7,975	35,381	55,340	15,321	20,620	16,938
Toilet	...	4,193	14,449	9,383	3,199	4,532	3,452
Soft Soap	...	...	...	78	42	265	76
Polishing and Scouring Soaps	...	...	...	107	41	...	60
Other sorts	...	...	...	2,790	652	3	60
Varnish [1]	6,517	2,262	9,634	8,974	1,936	1,181	1,691
Glycerine	...	84,718	168,742	94,513	Subdivided	...	...
Crude	...	...	...	...	49,843	54,872	65,181
Distilled	...	...	...	...	4	2,701	12,704
Rosin	...	14,690	65,292	148,302	49,251	56,327	52,835
Nuts and Kernels for expressing for Oil	...	292,250	672,328	1,076,918	539,182	472,875	436,404
Blacking and Polishes	...	4,761	14,378	14,450	4,984	6,724	5,736
Cattle Foods—							
Sweetened	...	...	935	461	547	1,587	2,232
Other sorts, not Oil Cake	...	...	64,200	143,039	18,600	13,974	22,514
Floorcloth, Oilcloth, etc.	7,308	5,110	12,941	Subdivided	since 1905	...	...
For Floors	...	...	...	8,883	1,781	2,728	1,426
For Furniture	...	...	...	1,286	206	1,260	780
For other uses	...	...	...	145	269	648	131
Paraffin Wax	...	14,860	72,987	76,502	41,255	44,445	79,272

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[1] Most varnishes are included under "paints."

TABLE III.—RE-EXPORTS—*continued*

	1913.	1914.	1915.	1916.	1917.	1918.	1919.	1920.
	£	£	£	£	£	£	£	£
Butter	584,674	510,148	318,437	232,368	69,836	13,498	28,306	419,065
Margarine and all artificial Butters	21,693	23,270	8,968	31,118	59,652	4,753	4,869	17,374
Cacao Butter	694	3,834	18,220	95,387	47,884	41	26,626	25,008
Oleomargarine	383,312	256,249	828,662	1,081,008	407,749	5,100	1,139,788	735,023
Lard	865,450	483,639	489,246	426,407	264,430	100,428	1,078,374	384,990
Imitation Lard	11,237	9,437	11,615	74,141	6,902	105	96,560	24,443
Oils—								
Fish, Train or Head Matter, Blubber, Sperm	121,360	99,216	107,759	37,784	178,897	31,820	321,394	252,612
Animal	10,310	7,175	7,516	6,888	7,620	1,250	342,313	70,307
Castor	1,674	428	1,277	6,270	1,944	17	6,619	4,591
Coconut—								
Unrefined	129,846	86,140	248,537	201,013	333,848	38,561	740,993	231,706
Refined	27,917	32,425	83,160	24,253	6,456	...	15	44,529
Olive—								
Unrefined	13,550	17,847	6,578	913	1,339	...	222,394	1,105
Refined	70,689	63,705	50,687	48,422	38,531	1,731	45,126	82,007
Palm—								
Unrefined	308,050	1,205,192 [1]	897,526 [1]	500,952 [1]	859,875 [1]	26,016 [1]	975,448	2,368,245
Refined	1,858	1,187	1,232	636	57	...	1,412	5,461
Seed Oils—								
Cotton Seed Oil—								
Unrefined	5,699	13,679	2,170	5,865	2,486	...	1,054	47,629
Refined	24,941	53,766	309,866	28,291	4,029	...	198,270	2,351
Linseed Oil—								
Pure	21,819	3,400	2,275	209	60	...	26,392	7,040 [2]
Not Pure	10	295	...	6	536	...	...	...
Rape Seed Oil	161	1,239	6,549	1,719	2,763	...	1,623	33,334
Other sorts	45,006	37,405	156,850	345,685	4,939	1,644	32,882	23,790

[1] Not including palm kernel.

[2] Including boiled oil.

Cotton	1,588	702	2,007	122	110	18	...	2,017
Linseed	69,695	164,088	235,090	12,765	1,969	2,629	278,918	55,629
Rape	3,772	69,477	169,412	190,070	195,231	...	570	129,439
Soya Bean	6,842	84,095	16,036	26,371	6	...	62	250,773
Castor	154,135	104,955	61,210	101,688	31,340	...	22,606	153,728
Other sorts	42,569	80,946	534,813	764,315	35,558	5,245	44,193	82,307
Tallow and Stearine	1,662,213	1,403,658	1,033,013	380,030	297,694	16,472	2,103,804	1,779,386
Candles	7,634	11,871	15,338	31,511	17,167	...	50,723	63,172
Oil Cake—								
Linseed	10,293	649	983	76	201	160	40,542	48,917
Cotton Seed	1,436	3,358	33,410	...	60	...	43,075	245,410
Rape Seed	...	225	1,671	...	...	...	...	48
Other sorts	9,495	14,164	28,802	78	21	...	124,341	9,727
Soap and Soap Powder	...	...	...	...	...	...	...	...
Soap (transparent)	139	118	15	12	...	...	...	...
Soap Powder	115	216	272	10	...	...	...	...
Soap Stock	4,476	15,745	287	...	...	...	...	...
Soap, Household	17,288	11,196	10,353	2,736	2,741	39	79,647	10,336
Toilet	4,652	2,507	4,087	2,674	809	1,197	2,639	14,062
Soft Soap	128	30	87	6	118	...	7	471
Polishing and Scouring Soaps	122	153	2,212	2,082	87	...	1,313	115
Other sorts	451	76	26	40	...	...	460	...
Varnish [1]	1,369	1,242	1,307	1,760	136	83	4,623	2,275
Glycerin	...	...	...	...	...	...	...	...
Crude	47,145	41,819	18,377	...	...	...	470	56,920
Distilled	2,416	314	4,072	23,090	...	...	...	217,860
Rosin	55,031	89,374	295,544	334,736	46,021	1,868	69,892	263,030
Nuts and Kernels for expressing for Oil	629,176	988,554	2,545,842	1,098,489	655,538	3,954	285,782	1,122,455
Blacking and Polishes	2,494	1,229	1,012	986	1,019	962	6,605	4,147
Cattle Foods—								
Sweetened	2,056	2,728	4,308	...	...	...	...	889
Other sorts, not Oil Cake	22,504	8,614	22,517	6,613	...	...	84,579	4,835
Floorcloth, Oilcloth, etc.—								
For Floors	1,630	912	...	4	...	...	119	...
For Furniture	772	1,239	85	90	74	...	41	114
For other uses	363	165	190	44	258	...	39	207
Paraffin Wax	81,311	110,584	177,274	233,444	94,632	800	287,650	431,894

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[1] Most varnishes are included under "paints."

TABLE IV.—SUMMARY

	1898.	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.
	£	£	£	£	£	£	£	£	£
Imports . . .	33,973,814	37,689,116	40,929,185	43,874,659	46,953,142	47,659,906	47,501,971	48,676,394	53,287,712
Exports . . .	3,785,002	4,215,227	4,804,370	5,032,143	5,501,008	6,299,108	6,336,235	6,752,289	7,716,119
	37,758,816	41,904,343	45,733,355	48,906,802	52,454,150	53,959,014	53,838,206	55,428,683	61,003,831
Less re-exports .	3,693,828	3,827,063	3,861,132	3,285,252	2,984,592	3,817,502	3,982,701	4,243,115	4,509,189
	34,064,988	38,077,280	41,872,223	45,621,550	49,469,558	50,141,512	49,855,505	51,185,568	56,494,642

	1907-9.	1910.	1911.	1912.	1913.	1914.
Imports	149,404,303	65,508,119	62,890,522	66,650,542	68,987,118	56,114,444
Exports	25,937,312	13,080,519	88,067,897	11,931,441	11,886,972	10,578,435
	175,341,615	78,588,638	150,958,419	78,581,983	80,874,090	66,692,879
Less re-exports . . .	19,019,289	7,485,381	6,728,295	6,310,629	6,494,160	6,624,679
	156,322,326	71,103,257	144,230,124	72,271,354	74,379,930	60,068,200

	1915.	1916.	1917.	1918.	1919.	1920.
Imports	82,030,181	83,170,795	83,499,425	103,578,472	147,774,584	126,062,087
Exports	12,316,651	11,780,546	13,634,739	7,475,301	28,510,431	30,175,166
	94,346,832	94,951,341	97,134,164	111,053,773	176,285,015	156,237,253
Less re-exports . . .	8,776,782	6,363,177	3,680,623	258,391	8,623,158	9,730,773
	85,570,050	88,588,164	93,453,541	110,795,382	167,661,857	146,506,480

Imports of Seeds and Oils into France (in 100 Kilos)

	1907.	1908.	1911.	1912.	1913.	1914.	1915.	1916.	1917.	1918.	1919.	1920.	1921.
Linseed	189,099	181,661	1,191,175	1,519,047	2,514,016	1,336,555	371,856	638,462	516,628	235,795	1,051,475	345,512	1,035,563
Rape seed, Indian	60,536	39,232	..	663,035[1]	538,477[1]	404,032[1]	137,717[1]	138,178[1]	159,946[1]	18,151[1]	308,338[1]	182,768[1]	53,007[1]
,, European	137	226	..	11,183	4,204	1,208	23	5	11	14	409	23,011	8
Navettes	217	12	8,999	40,306	12,923	6,885	47	...	54	2,272	11	3	1,090
Cotton seed	38,548	34,161	319,353	373,465	185,870	154,720	27,037	21,623	698	11,161	60,412	17,905	34,454
Hedge mustard seed[2]	485	228	..	..	..	..	..	..	..	..	..	..	..
Sesamé	68,502	51,234	1,026,168	213,817	278,166	261,266	160,080	597,511	366,351	22,742	320,895	469,096	75,755
Poppy seed	29,248	21,279	386	180,127	90,153	69,353	41,733	52,690	54,660	244	98,696	46,688	37,675
Copra	97,277	152,104	1,923,466	1,669,718	1,223,599	1,063,725	1,326,069	1,691,278	664,922	213,403	527,292	781,408	626,417
Arachis nuts	163,241	154,114	2,228,471	2,260,968	2,634,095	2,742,153	2,740,487	1,426,885	1,341,248	740,018	1,448,965	2,189,122	2,235,455
,, decorticated	117,404	84,807	2,199,957	2,598,150	2,686,783	2,984,539	1,397,979	2,299,043	1,041,344	94,439	827,639	1,800,562	1,498,264
Linseed oil	893	926	28,755	29,266	32,329	18,821	57,040	128,905	149,696	36,427	222,881	128,787	144,368
Rape oil	19	17	..	5,266	5,600	2,619	13,156	29,042	37,279	162	17,145	5,583	216
Cotton seed oil	34,059	46,750	114,131	150,669	120,272	64,325	151,540	64,528	73,155	21,396	59,374	113,855	80,797
Olive oil	21,356	30,581	232,923	537,381	238,558	396,938	226,865	372,130	601,371	131,589	676,266	111,629	296,967
Palm oil	16,087	17,841	229,400	219,226	212,831	183,620	262,581	375,044	239,767	145,108	261,503	409,661	89,416
Coconut oil	2,916	3,517	16,608	30,873	39,241	16,726	4,257	15,445	101,112	15,552	150,718	89,731	55,613
Arachis oil	825	111	973	2,919	4,807	382	13,529	62,539	25,945	10,051	44,075	100,245	49,430

Exports of Seeds and Oils from France (in 100 Kilos)

	1907.	1908.	1911.	1912.	1913.	1914.	1915.	1916.	1917.	1918.	1919.	1920.	1921.
Linseed	5,474	4,742	141,394	100,112	113,623	101,618	56,475	27,567	19,896	4,596	38,657	32,950	22,379
Rape seed	3,537	2,240	..	2,521	1,435	16,016	18,193	4,354	38	50	75	19,153	9,839
Poppy seed	315	41	5,001	953	1,047	1,015	158	107	..	..	1	..	..
Sesamé seed	1,031	3,459	68,643	31,629	75,917	42,057	28,164	5,674	703	606	1,141	9,084	14,689
Arachis nuts	8,955	10,584	205,961	176,603	236,228	170,534	87,303	32,305	7,622	5,898	10,697	37,074	70,875
,, decorticated	7,040	5,558	435,462	201,829	326,726	285,542	141,076	75,530	4,864	139	6,343	33,709	94,352
Linseed oil	4,144	2,550	88,854	57,577	51,515	35,764	45,168	34,725	27,892	19,024	26,140	28,595	17,931
Rape oil	2,361	1,548	..	23,590	25,672	20,043	8,455	6,816	4,007	896	3,634	9,351	16,265
Cotton seed oil	2,061	2,495	27,962	27,745	38,663	14,979	30,382	25,654	14,120	24,837	11,791	20,574	50,426
Poppy seed oil	298	381	9,475	5,404	4,776	5,349	499	135	8	13	28	167	506
Palm oil	291	650	46,252	28,228	19,324	11,604	18,145	41,167	10,600	7,679	14,632	32,671	16,206
Olive oil	..	..	167,428	220,194	222,094	211,870	126,869	122,704	72,199	32,111	85,981	98,934	133,163
Coconut oil	14,568	22,724	467,601	114,691	108,022	74,102	87,787	59,944	29,434	6,765	34,875	52,734	66,857
Sesamé oil	11,895	6,252	135,969	80,446	62,822	62,942	27,071	23,396	13,058	3,755	2,896	34,338	21,801
Arachis oil	6,260	6,457	206,650	209,452	269,979	224,134	296,241	150,774	70,106	23,202	29,597	139,964	414,744

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[1] Including hedge mustard seed.

[2] Included with Indian rape seed from 1912.

Imports of Seeds and Vegetable Oils and Fats into Germany (in 100 Kilograms)

	1907.	1908.	1909.	1910.	1911.	1912.	1913.	1920.
Rape seed, rubsen seed	1,567,370	697,542	1,427,025	1,873,024	1,344,531	1,256,836	1,534,269	886,906
Cameline seed, hedge mustard seed, radish seed	50,646	48,845	24,769	21,029	28,310	26,810	24,988	3,999
Poppy seed, sunflower seed	362,678	227,612	203,451	197,590	267,132	164,033	205,858	1,638
Madia, kapok, niger seeds	1,648	635	2,428	1,625	1,448	3,116	4,551	9,955
Sedge nuts, beechnuts, laurel berries	4,696	612	2,465	10,485	8,045			
Arachis nuts	250,500	236,186	499,094	691,330	701,425	698,695	980,853	99,516
Sesamé seed	668,254	729,691	779,401	1,413,965	1,016,710	992,818	1,160,386	249,885
Linseed (linseed meal)	4,398,597	4,684,218	4,368,667	3,205,224	2,763,431	3,300,928	5,603,232	530,590
Hemp seed	95,113	111,985	77,526	62,696	...	73,201	98,522	610
Cotton seed	404,891	525,281	934,282	1,062,324	1,557,850	2,140,969	2,197,969	5,216
Illipé nuts, mowrah seed	...	733	168,705	435,647	988,530	1,252,251	1,257,502	227,654
Shea nuts	...	...	73	...	...			
Castor seeds and soya beans	32,749	17,624	8,099	10,945	7,866			
Palm kernels	1,684,068	1,806,847	2,304,476	2,424,537	2,504,532	2,614,078	2,359,169	272,332
Copra	497,847	836,688	1,121,593	1,559,885	1,479,598	1,832,582	1,964,491	968,934
Coconuts	33,684	42,545	43,050	45,936	42,768	50,392	54,766	30,034
Rape oil	9,447	14,981	10,208	8,630	7,646	7,006	11,748	851,929
Linseed oil	27,945	17,446	20,589	19,069	28,648	26,880	31,648	
Beechnut, poppy, niger, sunflower, oils	643	469	429	519	468	110,775	31,399	
Arachis oil	7,355	6,595	10,105	10,558	5,228	10,465	5,142	
Sesamé oil	12,936	11,714	10,489	7,688	8,343	5,586	6,915	
Olive oil, pure	48,575	57,979	26,646	47,392	25,126	35,831	22,850	
Olive oil, lavate and sulphur oil	49,784	56,743	19,124	65,830	34,559	48,408	24,826	
Other oils, maize, neatsfoot, bone	...	57,132	63,455	141,791	249,714	53,451	33,904	
,, (in canister bottles)[1]	...	7,950	5,416	5,871	5,821	5,184	4,508	
Cotton seed stearine	...	6,461	10,306	3,485	2,074	1,850	4,144	
Cotton seed oil	527,707	440,694	343,368	184,348	216,725	268,744	162,778	
Tung oil	20,397	29,406	31,227	59,762	86,781	57,181	47,675	
Castor oil	56,775	62,500	84,934	86,080	94,863	85,847	95,267	684,031
Palm oil	130,075	95,429	152,356	160,335	128,888	118,734	150,717	
Palm kernel oil	1,134	618	397	666	1,640	56	485	
Coconut oil	35,864	50,759	90,490	89,062	22,834	3,333	5,944	
Shea butter and other vegetable fats	6,656	3,427	25,773	52,845	10,516	11,202	34,460	
Cacao butter	...	106	208	263	665	617	941	324
Oil cakes and seed meals	7,137,764	6,640,593	7,313,234	7,139,327	7,567,720	7,941,904	8,284,916	503,951

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[1] This is the official nomenclature.

Exports of Seeds and Vegetable Oils from Germany (in Metric Hundredweights)

	1907.	1908.	1909.	1910.	1911.	1912.	1913.	1920.
Rape seed, rübsen seed	81,942	62,126	51,926	92,828	69,833	70,968	49,729	159
Cameline seed, hedge mustard seed, radish seed	2,646	2,646	435	308	40	378	45	4
Poppy seed, sunflower seed	978	265	3,436	159	324	1,311		
Madia, kapok, niger seeds	28	50	34	50	125			
Sedge nuts, beechnuts, laurel berries	56	48	226	171	152		1,394	175
Arachis nuts	2,082	214	187	439	430			
Sesamé seed	34	106	799	9	15			
Linseed	59,313	84,093	68,280	115,615	63,435	53,989	42,317	3,335
Hemp seed	67,678	68,923	59,188	27,074	20,962	31,714	24,784	6
Cotton seed	57	282	2,019	1,919	14,958	18,021	8,095	2
Illipé nuts, shea nuts, mowrah seed	...	342	...	34	7,525	...	...	
Palm kernels	19,763	13,789	727	1,297	426	...	...	
Castor seeds, soya beans	3,168	315	3,748	2,905	565	...	...	
Copra	13,436	10,743	16,482	10,349	13,648	9,806	5,489	...
Rape oil	31,009	35,267	40,742	94,241	57,381	24,063	41,398	5,307
Linseed oil	12,069	8,854	6,265	45,307	32,228	9,527	5,744	
Beechnut, poppy, niger, sunflower, arachis, and sesamé oils	10,998	18,454	23,045	46,769	73,358	117,066	162,048	
Palm oil	...	471	1,079	2,043	1,162	772	395	...
Palm kernel oil	288,896	291,451	425,971	441,099	388,583	323,105	289,544	...
Coconut oil, shea butter, and vegetable fats	39,570	68,096	30,305	98,715	89,045	183,189	248,777	...
Cacao butter	...	18,494	27,905	22,465	36,105	36,426	19,593	4,732
Other oils and fats	...	18,375	23,045	46,769	73,358	...	...	...
,, ,,	...	7,545	8,473	13,374	11,910	...	...	...
,, ,, (in canisters and bottles)	...	2,002	1,688	2,571	2,891	...	...	...
Oil cakes, oil meal, and oil bran	1,797,111	1,890,736	1,962,530	2,043,884	2,332,347	2,636,226	2,941,738	34,428

Imports of Animal Oils and Fats into Germany (in 100 Kilograms)

	1907.	1908.	1909.	1910.	1911.	1912.	1913.	1920.
Lard	1,048,051	1,087.020	937,856	583,879	963,626	1,061,216	1,073,869	1,234,132
Oleomargarine	315,303	231,994	230,201	234,681	266,250	245,548	264,283	50,843
Goose fat, beef marrow fat, and similar fats	5,480	3,489	3,404	2,529	3,165	2,116	3,079	8,190
Premier jus	59,508	56,134	95,771	125,489	107,747	196,244	203,219	74,664
Beef and mutton tallow, pressed tallow	216,638	163,558	174,243	221,711	218,331	214,291	268,239	144,728
Bone fat, waste fat	45,367	28,125	29,553	25,664	35,076	27,403	43,157	43,310
Fish oils, seal oils	201,014	177,543	213,402	285,341	312,767	440,635	505,441	150,433
Oleine (oleic acid)	160,390	154,525	186,766	162,039	145,524	137,985	121,298	35,042
Whale oil, whale-bone oil, etc.	...	...	4,541	5,475	3,069	3,864	5,337	18,582
Margarine	...	...	953	907	976	198	192	...

Exports of Animal Oils and Fats from Germany (in 100 Kilograms)

	1907.	1908.	1909.	1910.	1911.	1912.	1913.	1920.
Premier jus	199	978	616	65	1	...	...	...
Beef and mutton tallow, pressed tallow	4,430	6,770	6,632	3,899	3,764	3,005	2,536	107
Bone fat, waste fat	88,815	105,946	87,869	95,738	90,459	92,044	80,028	1,521
Fish oils, seal oils	2,206	1,714	1,662	2,853	3,280	2,758	31,146	554
Oleine (oleic acid)	2,544	3,900	...	13,248	7,178	10,924	20,437	699
Margarine	...	...	5,207	82,919	175,895	4,916	1,816	...

Imports of Waxes into Germany (*in* 100 *Kilograms*)

	1907.	1908.	1909.	1910.	1911.	1912.	1913.	1920.
Vegetable waxes . .	5,945	7,409	9,805	9,664	8,956	5,099	5,852	2,122
Beeswax	18,352	18,039	18,248	21,643	26,668	29,993	29,535	
Spermaceti . . .	143	204	212	179	227	290	221	137

Exports of Waxes from Germany (*in* 100 *Kilograms*)

	1907.	1908.	1909.	1910.	1911.	1912.	1913.	1920.
Vegetable waxes . .	...	...	255	325	4,317	3,884	3,999	1,209
Beeswax	5,800	4,275	4,805	5,680	10,365	14,532	10,888	
Spermaceti . . .	13	2	2	4	5	7	4	3

A convenient classification of the oil and fat industries may be arranged under the following three heads :—

A.—INDUSTRIES HAVING FOR THEIR OBJECT THE REFINING OF OILS AND FATS AND THEIR APPLICATION TO COMMERCIAL USES.

B.—INDUSTRIES IN WHICH THE GLYCERIDES UNDERGO A CHEMICAL CHANGE, BUT ARE NOT SAPONIFIED.

C.—INDUSTRIES BASED ON THE SAPONIFICATION OF OILS AND FATS.

The industries dealing with *waste oils, fats, and waxes* will be considered in Chapter XVI., although the operations practised in these industries fall under one or more of the three foregoing headings.

A.—INDUSTRIES HAVING FOR THEIR OBJECT THE REFINING OF OILS AND FATS AND THEIR APPLICATION TO COMMERCIAL USES.

The general methods of refining and bleaching have been outlined already in Chapter XIII. Those methods which apply to individual oils and fats have been considered in the foregoing chapter under the separate heading of each oil and fat which is purified on a commercial scale. The method of refining, and the degree to which it is carried, depend, of course, on the purpose which the oil and fats are intended to serve. Therefore, the methods must be adapted to each individual case, as has been pointed out already.

I.—EDIBLE OILS AND FATS

Oils and fats which are intended to serve as food are chiefly purified by physical methods. Chemicals involving the use of mineral acids must be altogether excluded from the purview of the refiner, since the mineral acids, however carefully they may be removed by subsequent washing, impart an objectionable flavour to the products treated, thus rendering these useless for edible purposes. Alkalis or alkaline earths are not so objectionable, and are therefore used commercially for the removal of free fatty acids. A notable example of this kind is furnished by the usual method of refining cotton seed oil. The alkalis and alkaline salts chiefly employed in practice are caustic soda, sodium carbonate, lime, and magnesia. Baryta has also been proposed (and patented), but its poisonous properties would prohibit its use.

As other neutralising agents there have been proposed ammonia [1] and also sodium silicate.[2]

In the case of alkaline salts the stoichiometrically calculated quantities do not suffice to convert the free fatty acids completely into soaps, a considerable excess of alkaline salts being necessary to effect complete neutralisation. Frequently extremely persistent emulsions are formed, the successful "breaking" of which requires great circumspection and experience. No general rule can be laid down, different oils and fats demanding different treatment. Frequently the application of heat or addition of salt leads to the breaking up of the emulsion, but in either case only the observation of the minutest details will assure success. The "breaking" of the emulsion is also stated to be effected by treating the mass for a short time under steam pressure, after having admixed some carbon or fuller's earth or "infusorial earth" to counteract the detrimental action of air, heat, and pressure.[3]

The neutralisation of the free fatty acids by means of an alcoholic solution of caustic potash and subsequent removal of the soap formed by washing the oil with alcohol has been described by *Hermann*.[4]

If *lime* is used the emulsion is sometimes so persistent that the whole mass must be evaporated down in vacuo, when the lime soap, on becoming anhydrous, separates out in granular form, so that it can easily be removed from the oil by decantation or, better still, by filtration.[5] No excess of lime must be used, or saponification of the neutral fat may occur. It is, however, stated by *Jüssen* [6] that if the fats are treated at about 100° C. with dilute milk of lime, finely pulverised by means of a steam injector, the free fatty acids only are acted upon without saponification of the neutral fat taking place. It has been further stated that under these conditions the combination of lime with fatty acids takes place with the theoretically required quantity of lime.

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[1] P. Piek, German patent 166,866.

[2] Godard, English patent 22,085, 1903.

[3] Fresenius, French patent 325,768; English patent 19,171, 1902; German patent 143,946. In a second patent (French patent 354,810, 1905) the pressure is reduced to 1½ atmosphere, the temperature is kept at 85° C., and the pressure is produced by an indifferent gas, carbonic acid, or nitrogen (cp. English patent 9105, 1893). Thus a "preservative" like char, etc., is said to be no longer required.

[4] French patent 348,010.

[5] Ruffin, French patent 253,417; German patent 90,521, 1897. Soc. anonyme des Savonneries de la Méditerranée, French patent 327,581.

[6] German patent 125,993.

Neutralisation by means of magnesia has been proposed by *Jeserich and Meinert-Bünau*.[1] This process gives useful results in certain cases (see "Vegetable Butters," below).

It cannot be stated too emphatically that it is not possible to propound general methods which are adaptable to all cases, and that the art of the refiner consists in choosing those conditions which are found by careful experiment to be the most suitable in each individual case. Since most of the processes mentioned above have been worked out chiefly for coconut oil (see below), the very large number of publications claiming to effect successfully the complete de-acidification of oils and fats must be read with due reserve.

The production of edible fats of tallow-like consistence from cotton seed oil, maize oil, soya bean oil, and the like by a process of hydrogenation in the presence of a metallic catalyst has already reached large proportions.[2] The hardening of whale oil for the purposes of margarine making is taking place in Germany, where, however, medical opinion was strongly against its use [3] (see below, p. 124). If hardened vegetable oils are suitable for edible purposes it is difficult to see the objection to hardened whale and fish oils, provided, of course, that they are properly refined before hardening. In this connection it may be noted that fats of a very high melting point are not completely digested. In cases where hardened fat is suspected, the ash must be carefully examined for traces of the metallic catalyst (cp. Vol. I. p. 298).

The *physical methods* imply, in the first instance, boiling with water, or treating with a current of finely divided steam, whereby volatile substances, which impart to the oils and fats an unpleasant taste or odour, are removed. This process is technically known as "deodorisation," and was already applied in 1814.

The application of steam for deodorising was a distinct improvement on the process of heating the oils and fats to a high temperature, a method which appears to have been proposed first by *Dubrunfaut*, and has been recently repatented for the deodorisation of fish oils.[4] Later *Dubrunfaut* himself recommended a current of steam to drive off the volatile fatty acids, and since the middle of the last century steam has been frequently employed (and patented) for this purpose, the steam being used either at low pressure or at high pressure, or at low pressure and in vacuo,[5] and as superheated steam.

A process for the deodorisation of oils by directing a current of the atomised oil against a blast of air has been patented.[6]

Since in the hot state oils and fats are especially liable to oxidation and hence to rancidity, recourse has frequently been had to the exclusion of air and its substitution by an indifferent gas.[1]

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[1] German patent 19,819, 1882. Chevreul used sub-carbonate of magnesia in 1813.

[2] Déveaux, French patent 458,611.

[3] Cp. Böhm, *Seifensiederzeit.*, 1912, 1078.

[4] E. Böhm, English patent 7901, 1906 (cp. Vol. II. p. 420).

[5] Schlinck, United States patent 653,041; Petty, English patent 16,954, 1892.

[6] Casamajor, French patent 384,492.

The deodorised oil or fat is allowed to rest for some time so that any occluded water may separate out. It is then filtered in order to remove the last traces of water and suspended matter. If it be required to remove small amounts of colouring matter, the materials are treated with charcoal or fuller's earth or hydrosilicate (" decolorised ") and filtered through a filter-press.

For further information the patent specifications referred to in the footnote may be consulted [2] (cp. also p. 57).

Animal fats intended for edible purposes should be rendered from the tissue before it has had time to putrefy, as the decaying tissue gives rise to ptomaines.[3] The same remark applies to vegetable oils, which can acquire poisonous properties if left in contact with mouldy seed.

1. EDIBLE OILS, SALAD OILS, SWEET OILS

French—*Huiles à bouche, Huiles comestibles, Huiles de table.*
German—*Tafelöle, Speiseöle.* Italian—*Olii da tavola.*

Most of the **vegetable** cold drawn oils, if prepared from fresh seeds or fruits, are suitable for edible purposes, as also for the preservation of food stuffs (*e.g.* olive oil in the sardine tinning industry). Hence, practically every vegetable oil, with the exception of those containing toxic substances (cp. tung oil, candle nut oil, calophyllum oil, castor oil, curcas oil, croton oil, and also the oils from *Byronia dioica* and *Cytisus laburnum*, and the oils belonging to the chaulmoogra group) or unpleasant ethereal oils like mace butter, may be, and indeed is so employed, as has been pointed out already in Chapter XIV. Naturally, much depends on the demand made as to palatableness by the population in the various countries of the world. Thus, whereas rape oil and linseed oil find a ready market for edible purposes in India, these oils are at present only used in exceptional cases as table oils in Western Europe. They are replaced in richer countries by cotton seed oil, sesamé oil, arachis oil, poppy seed oil, and olive oil.

In the manufacture of edible oils the chief attention must be devoted to the removal of free fatty acids.[4] For this purpose alkalis and alkaline earths are almost exclusively used. Conjointly with the free fatty acids there are also removed natural impurities, such as mucilaginous and albuminoid substances, which are instrumental in bringing about hydrolysis (Vol. I. Chap. I.) and thus give rise to the formation of free fatty acids and to rancidity, which follows in the wake of hydrolysis.

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[1] C. D. Abel (from *Fabriques de produits chimiques de Thann et de Mulhouse*), English patent 9105, 1893; French patent 228,475, 1893.

[2] Rocca, English patent 10,899, 1900; German patent 127,492; United States patents 699,571, 699,572; French patent 325,381; Godard, Belgian patent 163,411, 1902; English patents 22,085, 1903; 22,086, 1903; the corresponding French patents 338,677 and 338,678 are taken out under the name Soc. anon. des Usines J. E. de Bruyn, Termonde, Belgium.

[3] Bontoux, *Les Matières grasses*, 1911, 2160.

[4] E. R. Bolton and E. J. Lush patent a method for converting the free fatty acids into glycerides, English patent 163,352, 1921.

It is of great importance that table oils should not congeal at temperatures near the freezing point. Olive oil practically fulfils this demand, with the exception of some Tunisian olive oils from Sfax, Sousse, Mahdia, Monastir (see Vol. II. Chap. XIV.), which must be "demargarinated," in the same manner as is done in the case of cotton seed oil, before they can be placed on the market.

Arachis oil stands in this respect midway between olive oil and cotton seed oil (cp. "Arachis Oil," Vol. II.). From cotton seed oil, which is at present used in enormous quantities as an edible oil (as also for adulterating high-class edible oils), a considerable portion of "stearine" separates out at a temperature of about 40° F. In order to render cotton seed oil suitable for the table, *i.e.* to produce a "winter oil" (Vol. II. Chap. XIV.), the "stearine" must be removed, or, as the technical term runs, the oil must be "demargarinated." Originally the process of demargarination consisted in simply storing the oil in large vessels during the winter, when the "stearine" settled out as a solid mass at the bottom of the vessels, so that the supernatant clear oil, freed from most of the stearine, could be drawn off. This process must still be employed in the case of arachis oil (Vol. II. Chap. XIV.). Owing to the large amount of capital locked up, this process would be too expensive for cotton seed oil, enormous quantities of which are required by the market. Hence, in modern establishments the oil is refrigerated artificially, and the "stearine" removed by filtering or pressing (Vol. II. Chap. XIV. p. 203).

In commerce "edible oil," or "table oil," no longer denotes any one oil, unless it be specifically sold as such. It frequently represents a "blend" of several edible oils, such as cotton seed, sesamé, arachis, and olive oils. Hence, a blend of the kind just mentioned cannot be termed "adulterated olive oil" unless it has been sold as olive oil. Table oils sold under fancy names are, as a rule, "blends." Salad oils in Canada containing cotton seed oil must have the presence of that ingredient stated on the label. In the United States the term "salad oil" is held to denote pure olive oil exclusively.

The examination of the individual oils and the detection or adulterants has been treated at length in the foregoing chapter (cp. especially for organoleptic methods, limpidity, etc., Vol. II. Chap. XIV., "Olive Oil").

After the nature of an edible oil has been ascertained (*i.e.* whether free from adulterants,[1] if it be sold as a specific oil), the estimation of the free fatty acids is required to complete the examination.

No rule can be laid down as to what should constitute the permissible maximum of free fatty acids in a salad oil or culinary oil (for frying fish, etc.), the limit naturally depending on the demand made as to taste and palatableness in the various countries or localities.

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[1] A table oil consisting of a "blend" of several oils, such as arachis and olive oil, or cotton seed and olive oil, is not necessarily an adulterated oil.

It may, however, be stated that a perfectly neutral oil has an insipid taste, and that therefore an oil must not be judged unsuitable for edible purposes for the single reason that it contains about 1 per cent of free fatty acids. Edible cotton seed oil being refined by means of alkalis or alkaline earths will usually be found to contain much less than 1 per cent of free fatty acids. For the experiments on the nutritive value of fatty acids see *A. Lauder and T. Fagan.*[1]

In addition to all chemical tests, even provided they are satisfactory, the valuation of an edible oil must be based on its *taste*. If an edible oil be found rancid, it must be condemned as unfit for consumption. Therefore, the various methods that are being devised with a view to determining chemically the " degree of rancidity " of edible oils appear to the author to be somewhat superfluous. Moreover, it must be borne in mind that an unpleasant taste is not always attributable to the presence of free fatty acids and their oxidation products, other substances which are mostly present in small or even in the minutest quantities, also imparting an unpleasant flavour to an oil.

Whereas it is comparatively easy to decide whether an oil is rancid, and hence unfit for consumption, the valuation based on the flavour of an oil can only be made by one who possesses considerable experience. This applies, especially to edible olive oils (see Vol. I. Chap. XI., and " Olive Oil," Vol. II. Chap. XIV.), and to edible arachis, sesamé, poppy seed, and cotton seed oils.

Less rigorous demands as regards taste and flavour are made upon edible oils which are used for cooking and similar purposes. Thus the finest brands of rape oil are extensively used as " *bread oils*," the slightly burning taste, which would render this oil objectionable as a high-class table oil, disappearing during the progress of baking. An edible oil examined by *Rounet*[2] consisted of 34 per cent of a mixture of poppy and sesamé oils with 66 per cent of a mineral oil.

Diedrichs[3] recommends for the refining of vegetable oils a process involving the partial neutralisation of the free fatty acids followed by steaming with superheated steam under reduced pressure, and states that the oils so treated were much improved in flavour, whereas the oils steamed without previous removal of the free fatty acids, although deodorised, still retained a bitter after-taste.

Animal oils are not used alone for edible purposes, although lard oil finds a limited outlet in the manufacture of margarine. Hitherto it has not been possible to refine **fish oils** and free them from their peculiar fishy odour to such an extent as to render them fit for the table. Even for cooking purposes fish oils are not employed, although it would seem that, if suitably refined,[4] there should be an outlet for them in the sardine tinning trade (where olive oil, arachis oil, and other oils are chiefly used) or for fish-frying purposes, for which cotton seed oil (and in France sesamé oil) is largely employed.

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[1] *Journ. Soc. Chem. Ind.*, 1917, 1069.

[2] *Ann. d. falsif.*, 1909, 220.

[3] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912, 208.

[4] Cp. Lewkowitsch, " Problems in the Fat Industry," *Journ. Soc. Chem. Ind.*, 1903.

Cod liver oil only would seem to fall under this head, although it is exclusively used for medicinal purposes. Before the medicinal cod liver oils had reached the excellence they have now acquired in consequence of the application of modern methods of preparing and refining, an attempt was made to improve their taste, or at least to render the oil more palatable, by impregnating cod liver oil with carbonic acid. The oil was saturated with this gas under pressure, so that as soon as the latter was released the oil effervesced.

The process for preparing such **effervescent oils** (French—*Huiles effervescentes.* German—*Brausende Fette*), of which effervescent cod liver oil represents a type, has been patented.[1]

2. EDIBLE FATS

French—*Graisses alimentaires, Graisses comestibles.* German—*Speisefette, Kunstspeisefette.* Italian—*Grassi da tavola.*

Many edible fats, such as suet (tallow), lard, butter, cacao butter, goose fat, etc., are fit for consumption if prepared with sufficient care, and therefore rarely undergo a process of technical purification before they are placed on the market. Their preparation has been described in the preceding chapter; here only those edible fats will be considered which are produced on a manufacturing scale as substitutes for the natural products. These edible fats are artificial mixtures of different oils and fats. This applies especially to the first three classes of edible fats considered below.

From a sanitary point of view no objection can be raised against the substitution of the cheaper animal or vegetable fats for the more expensive ones, as long as these substitutes are sold *under their proper names*, and *are not* used for fraudulent purposes. It is rather to be desired that the industry of fat substitutes should extend further, yielding, as it does, cheap, palatable food-stuffs, and thereby tending to exclude from consumption the unwholesome fat from diseased animals, or at least fats which are prepared under conditions that do not satisfy the most rigorous demands as regards cleanliness.

The enormous strides which this industry has made during the last few years have shown that the popular prejudice which at first militated against the legitimate expansion of this trade has now been overcome. Nay, the excellence of the products has even reacted favourably on the antiquated methods of producing lard and butter, and has thus helped to introduce much needed improvement in the preparation of these food-stuffs.

The quality of an edible fat, irrespective of the nature of its components, depends in a great measure, if not solely, on its palatableness. Some writers are of the opinion that an edible fat should be declared unsuitable for consumption if its free fatty acids exceed a certain percentage, but any such rule must appear an arbitrary one. Although the determinaton of the amount of free fatty acids should not be omitted, yet the valuation of an edible fat cannot be based on the amount of the free fatty acids it contains. Taste alone must decide whether the amount of free fatty acids is excessive.

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[1] Chemische Fabrik Helfenberg, German patent 109,446, 1899; J. Barclay, English patent 11,410, 1902.

The question as to the digestibility of an edible fat hardly falls within the province of a chemist; still, it may be pointed out that *J. König*[1] takes objection to *A. Mayer's*[2] and *A. Jolles'*[3] statements that margarine is just as easily digested as is butter fat, and that both fats have the same nutritive value. Although *König's* opinion is being contested by *Lührig*[4] on the strength of a physiological experiment, it has been shown by prolonged observations (*Leffmann*[5]) that the substitution of butter in the diet by margarine resulted in a greatly diminished[6] consumption of fat. These conflicting opinions may be due to the nature of the fat experimented with, inasmuch as *W. D. Halliburton and J. C. Drummond*[7] have shown that oleomargarine, and consequently margarines, prepared with this as a basis contain the accessory substances necessary to growth, and are therefore comparable in this respect with butter. Coconut oil, cotton seed oil, arachis oil, and hydrogenated oils are deficient in these bodies and are unsuited to form the sole source of fat for human diet.

The author subdivides the edible fats into the following four groups :—

(1) Suet Substitutes.
(2) Butter Substitutes.
(3) Lard Substitutes.
(4) Cacao Butter Substitutes, Chocolate Fats.

(1) SUET SUBSTITUTES

French—*Succédanés du suif*. German—*Präparierter Talg, Bratenfette.*

Under the names "beef-lard," "lard-beef," "lardeen," etc., a number of cooking fats are sold as substitutes for "suet" or "dripping." They consist, as a rule, of a mixture of suet (tallow) and cotton seed oil or cotton seed stearine, and are prepared by simply intermixing the melted ingredients in a mixing machine and stirring until the material has acquired, by spontaneous cooling, a salve-like consistence.

A mixture of beef stearine and cotton seed oil (20 parts of beef stearine and 80 parts of cotton seed oil) can also be prepared on "lard coolers," the mixture being brought to a temperature slightly above the crystallising point of the stearine. In this case (as also in the case of compound lards) it is important to avoid the product becoming unctuous and semi-transparent, which would indicate that the mixture will separate in course of time by a kind of liquation process into oil and stearine.

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[1] *Die menschlichen Nahrgs- u. Genussm.*, 2nd ed. 2, 306.
[2] *Landw. Versuchst.* 29, 215.
[3] *Milch-Zeitung*, 1894, 670. "Über Margarine" (pamphlet), Bonn, 1895.
[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1899, 484, 622, 769; 1900, 73.
[5] *Second Annual Report of the Dairy and Food Commissioner of Pennsylvania.* Cp. also B. Fisher, *Wagner's Jahrbuch*, 1898, 970.
[6] Cp. also R. Kayser, *Zeits. f. öffent. Chem.*, 1899, 101.
[7] *Journ. Physiol.*, 1917, 51, 235; *Journ. Chem. Soc.*, 1917, 112, 1,673.

According to the prices ruling in the market for cotton seed oil, its proportion in the final product varies. If the amount of cotton seed oil be large, tallow of a high titer test, or even beef stearine, must be employed. The natural yellow colour of cotton seed oil imparts to the mixture the desired coloration.

If it be required to ascertain the amount of cotton seed oil, the determination of the iodine value will give the readiest answer.

On the Continent a similar cooking fat is being sold under the name "Schmelzmargarine" (cp. "Schmelzbutter," Vol. II. Chap. XIV.), this being the fatty matter obtained on melting margarine and separating it from water after allowing the latter to settle out (cp. also "Lard Substitutes," p. 58). For the production of such "Schmelzmargarine," which is usually free from water and casein, lower qualities of material may be employed as the fats are used exclusively for cooking.[1] *Stadley* protects [2] an edible fat consisting of butter, veal fat, lard, mutton fat, beef fat, sesamé and cotton seed oils.

When the price of edible tallow was high, frequent attempts were made to refine lower qualities of tallow by removing the free fatty acids and, to some extent, the "tallowy" odour. Since these products possess the natural white colour of tallow, they were usually coloured yellow (with regard to the detection and identification of colouring matters see Vol. II. Chap. XIV. p. 808).[3]

More recently, suet substitutes consisting of mixtures of tallow and coconut oil have been placed on the market. In some parts of Germany beef suet substitutes prepared from **linseed oil** and tallow, or linseed oil, tallow, and lard, have been brought into commerce under the name of "linseed oil lard" ("Leinölschmalz").

A process for deodorising fats intended for edible purposes has been patented by *Szigetvary and Magyar*.[4]

(2) BUTTER SUBSTITUTES

(a) Margarine, "Oleomargarine" [5]

French—*Margarine*. German—*Margarine, Kunstbutter*.
Italian—*Burro di margarina*.

The industry of butter substitutes owes its origin to experiments (induced by a prize offered by the French Government in 1869) made by *Mège-Mouriès*, which were worked out to a manufacturing process in Paris in the year 1870.

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[1] Strunk, *Veröffentl. a. d. Gebiete d. Militär-Sanitätswesens*, p. 65.

[2] English patent 10,429, 1910.

[3] Cp. also Sprinkmeyer and Wagner, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, ix. 598; Arnold, *ibid.*, 1905, x. 239; Fendler, *Chem. Rev.*, 1905, 208, 236; Fritzsche, *ibid.*; Pollatschek, *ibid.* p. 285; Crampton and Simmonds, *Journ. Amer. Chem. Soc.*, 1905, 270; Olig and Tillmans, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1906, xi. 94.

[4] French patent 445,202.

[5] This is the American term for our "margarine." The American equivalent of the term oleomargarine as used in this country is "oleo oil" or "margarine oil."

The most important conditions to be observed in the margarine industry are the employment of the freshest and purest materials and the utmost cleanliness in all manufacturing operations.

Margarine, "oleomargarine" (older names partly suppressed by legislation are "butterine," "Dutch butter"), consists either of a mixture of animal fats alone or of animal and vegetable oils and fats churned with cow's milk to a butter-like emulsion, and coloured yellow (unless forbidden by law)[1] with annatto, methylorange, etc. The cow's milk is sometimes replaced by an emulsion prepared from the kernels of almonds[2] or from soya beans, so that it is possible to prepare a margarine from vegetable products exclusively. The animal fats used are oleomargarine—"oleo oil"—and (or) neutral lard (the latter is almost exclusively used in the United States). Both ingredients must be prepared from the freshest beef fat and (or) hog fat respectively.

For margarines made exclusively of vegetable fats and oils see below.

For the production of oleomargarine, the rough fat is removed from the slaughtered animal as quickly as possible and brought immediately into the works, where it is sorted. The kidney and bowel fats are selected, then carefully washed with warm water and thoroughly cleansed. The cleansed fat is brought immediately into large, well-aired, artificially cooled rooms to dry and harden (being allowed to hang there suspended from tin hooks for several hours), or is immersed in iced water in order to secure more rapid hardening. The hardened fat is then cut up and shredded in a shredding machine, and finally ground between rollers.[3] The disintegrated mass is immediately introduced into tin-lined, jacketed vessels (melting kettles), and brought to a temperature not exceeding 42° C., this temperature being maintained by steam or hot water passing through the jacket.

At this temperature a portion only of the tallow contained in the tissue separates on the top of the comminuted rough fat. The settling and clearing is assisted by sprinkling salt over the surface of the melted fat. This melted portion, appropriately termed "premier jus," is run off into shallow tin-lined trays arranged in tiers in a cooled room, when the bulk of the "stearine" separates out in a crystalline condition. The crystallised mass in the tins is cut up into square pieces of about 3 lbs. weight each, wrapped in canvas cloths, and placed in hydraulic or mechanical presses.

For the best qualities of margarine, the "premier jus" is remelted at a temperature not exceeding 45° C. and allowed once more to settle out, after salt has been added, whereby the last remnants of membrane and tissue are precipitated. In large works the clear fat is allowed to run into wooden vats, in which it stands for from three to five days at a temperature suitable for the crystallisation of the "stearine." The whole is then stirred up into a homogeneous pulpy mass; this is wheeled in wooden waggons to the presses and treated as described already.

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[1] Cp. footnote 4, p. 36.

[2] Cp. Li Yu Ying, Belgian patent 231,588.

[3] Cp., *e.g.*, German patent 200,538 (E. Lange); *Chem. Rev.*, 1909, 39.

The oleomargarine, "oleo oil," which runs out from the presses, forms the chief raw material for the manufacture of margarine.

The "stearine," "oleostearine," which remains in the press is used in the manufacture of "lard substitutes," "suet substitutes," for "stiffening" lard, and even in the production of margarine, replacing part of the "oleo oil" in case the proportion of the vegetable oils demands the stiffening of the fat stock. Such addition of "beef stearine" must, however, be kept within proper limits, as otherwise the resulting margarine would lack in "richness" of taste.

In some works the rough fat from which the "premier jus" has been taken off in the manner described above is heated once more to about 50° C., when a second portion of fat is recovered. This is sold as "secunda jus," and is used in the manufacture of inferior kinds of margarine ("secunda" margarine). "Secunda premier jus" is a term given by continental makers to the "jus" obtained from caul fat (Vol. II. p. 765); such makers also term their "premier jus," if "sweet," "primissima jus."

The mode of producing neutral lard has been fully described under "Lard" (Vol. II. p. 700).

Amongst the vegetable oils, cotton seed oil and cotton seed stearine, sesamé oil, arachis oil, and even soya bean oil take the most prominent place. According to the intended quality of the margarine the quality of the cotton oil used varies. In any case the cotton seed oil must be practically devoid of free fatty acids, and rendered as free as possible from the peculiar flavour characteristic of this oil. The best brand of cotton seed oil used for margarine making is known under the name "butter oil." Arachis oil (also olive oil) and sesamé oil are used to a greater extent in Europe than in the United States. Recently, refined coconut oil and palm kernel oil (see (β)) is being incorporated with the fat stock of margarine.

The oleomargarine, "oleo oil" (and neutral lard), is mixed in churning machines, at as low a temperature as is consistent with a semi-fluid condition, usually between 25° and 30° C.[1] with the vegetable oils and fats, and with milk.

The quality of the resulting product depends to a great extent on the quality of the milk and on its treatment previous to its admixture with the fats. The milk may be either sweet milk or sour. Sweet milk is more difficult to amalgamate with the oils and fats, and is retained with greater difficulty than is soured milk, but the advantage the employment of sweet milk offers is that the resulting product has a finer taste and keeps better. The soured milk is however more easily incorporated with the fats and gives a higher yield. The proper treatment of the milk in the margarine works constitutes one of the most important features, just like the corresponding part of the butter-making process does in large dairies. The milk should be worked up as soon as possible after arrival. In any case it should be pasteurised immediately after its arrival, and no preservatives—not even salt—

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[1] W. Clayton, *Journ. Soc. Chem. Ind.*, 1917, 1205.

should be used to prevent the fermentation of the milk.[1] Stress must be laid on the necessity of working with pure cultures. Although these are obtainable of excellent purity in commerce, the propagation (dilution) of the starter and the excising of the culture requires careful bacteriological supervision. The use of ozone for sterilising milk has been patented.[2] Twenty minutes' heating of the milk to 60° C. is stated to be sufficient to destroy the tubercle bacillus.[3] If the cream has not been taken off before the milk reaches the margarine works, it is removed (for butter making) by means of a centrifugal machine, etc. The regular determination of the fat in the milk is necessary, not only for the proper control of the works, but also for the further reason that it has not infrequently occurred (on the Continent) that too much cream is taken off by the seller and replaced by sesamé oil, cotton seed oil, or even by margarine. Directions as to the proper souring of the milk fall outside the scope of this work,[4] although it may be noted here that *Richmond and Huish*[5] state that the organisms which normally cause the souring of milk are not those whose normal habitat is milk, and it is not improbable that they are of intestinal origin.

In place of cow's milk, kephir milk or even kephir fungus have been recommended (and patented [6]). It is claimed that the margarine so obtained has a full butter flavour and "browns" on being heated.

The churning machines consist of oval jacketed vessels provided with one or two sets of stirring and mixing gear. During the process of churning a constant temperature must be maintained by means of steam sent through the jacket of the churn. The object of churning, besides thoroughly mixing the ingredients, is to destroy the tendency of the oleomargarine to crystallise, and to pulverise ("atomise") the mixture, as it were, into single globules, such as butter fat forms in milk. The art of the margarine maker at this stage of the process consists, therefore, in carefully regulating the inflow of milk and fat stock, so that a thorough emulsion is finally obtained.

First the milk is put lukewarm into the churn and is mixed up with a little cream, followed by the addition of butter (if any be added). When the mass is properly emulsified,[7] part of the oleomargarine is added carefully, and when this has been properly incorporated with the emulsion, the oils required for the margarine stock are entered gradually, and only then the remaining oleomargarine is mixed in.[8] At this stage some manufacturers add colouring matters. The steam is then turned off and the warm material is cooled to a definite temperature by cold water being sent through the jacket.

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[1] French edition: For sour milk used in North Germany and Holland 1·5 to 3 per cent of salt is added.

[2] Freund, *Chem. Zeit.*, 1911, 906.

[3] Mohler, Washburn, and Rogers, *Report of the Bureau of Animal Industry*, 1909, 187.

[4] Cp. Vol. II., "Butter fat."; Jensen, *Zentralbl. f. Bakteriol.*, 1911, (ii.) 610; Eberlein, *Zeits. f. angew. Chem.*, 1911, (27) 1282.

[5] *Analyst*, 1912, 168.

[6] Pollatschek, German patent 140,941, 1902; K. Mann, English patent 15,311, 1905; German patent 179,186, 1904; United States patent 880,316.

[7] An improved apparatus for ensuring a complete emulsion has been patented by W. Fette, German patents 219,973, 237,737.

[8] A special *modus operandi* for producing a proper emulsion at 18°-20° C. has been patented by Pellerin, French patent 361,614, 1905; cp. also Blichfeldt, English patents 4505, 7498, 7499, and 8227, 1912, and 18,048, 1914.

From the churn the cooled margarine is run into cooling tanks, which are built up of marble or white tiles or simply consist of large wooden tanks. Whilst running out, the margarine is met by a current of ice-cold water, delivered under high pressure, in order to pulverise the mass thoroughly. The disintegrated globules, after solidifying, somewhat resemble butter granules.[1]

The cooling of the still liquid margarine by running it on to a cooled table (cp. *L. B. Doukers*, German patent 101,207) has the serious drawback that the cooled mass is of uneven thickness and hence an unevenly cooled product. This drawback is avoided by *E.* and *H. H. Schou*,[2] who cool the margarine in a thin layer of a thickness of about 1 to 1·5 mm. between two hollow cylinders which revolve in opposite directions and are cooled by a cold brine solution (cp. also " Lard Coolers," Vol. II. p. 702). A cooling machine in which the fat is spread in a thin layer on a cooled drum has been patented.[3]

A process intended to replace the expensive cooling by iced water and consisting in passing the warm margarine into a closed vessel, where it is cooled by a current of air,[4] offers some objectionable features, and therefore does not appear to have met with favourable reception in margarine works.[5]

A process for producing fats in the form of powder by incorporating with them a malt extract has been patented by *Hamburg*.[6]

During recent years a large number of patents have been taken for " homogenising " or " atomising " the mixture of milk and oils and fats in special machines.[7] The merit claimed for these machines is that the product is more solid and has no " oily " but " rather a nut-like " taste. The important demerit of all these apparatus is, however, that the margarine retains more water, and hence the proportion of fat falls below 80 per cent. Therefore in those countries where the maximum percentage of 16 per cent of water is prescribed by law the sale of such margarine must meet with difficulties. In order to obviate this drawback and at the same time to dispense with the kneading machines, in which the excess of milk is removed, *Schroeder*[1] carries out the blending and emulsifying process in three churning machines arranged one above the other and working in conjunction with an "atomiser." The temperature in the three churns through which the mixture of fats and milk passes is regulated carefully so that the completely emulsified contents of the lowest churn can be discharged on to a cooled table, where the mass solidifies to a thin layer, which is scraped by a tangentially acting "doctor" so that the thin solidified film is curled up and discharged into a waggon. The ingredients forming the margarine are therefore mixed in the proportion of 80 parts of mixed fats and oils, 16 parts of milk and 4 parts of cream consisting approximately of one-third of butter fat. An emulsifying machine, primarily intended for the manufacture of cod liver oil emulsions, has been patented by *Boothroyd and Woolliscroft.*[2]

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[1] Other arrangements have been patented by the Altonaer Margarine Werke, Mohr and Co.; French patent 408,917, 418,869; English patent 1227, 1910.

[2] French patent 379,905; German patent 197,004. Cp. also *Chem. Revue*, 1908, 190, and English patents 5810, 1908; 1160, 1909; French patent 454,640; Belgian patent 254,019, and English patent 23,467, 1913 (E. V. Schou). Cp. Flakes, Ltd., vol. iii.; Rasmussen, German patent 272, 846.

[3] Korsör, *Margarine fabrik Aktieselskam*, English patent 29,564, 1910; Jamieson, English patent 20,292, 1912; Rasmussen, English patent 29,831, 1910; Christensen and Vang-Lauridsen, English patent 20,568, 1912.

[4] Scheffel, German patent 116,755 (1899); Weber-Liel, German patent 240,291; Schlinck, German patent 257,790.

[5] Cp. N. M. Risberg, English patent 25,890, 1907; German patent 222,529; French patent 396,450.

[6] English patent 29,481, 1912.

[7] D. F. de Kierzkowski-Steuart, English patent 27,618, 1904; G. Kunick, German patent 166,935; Deutsche Homogenisiermaschinen Gesellschaft, Lübeck, French patent 354,943; German patent 189,415; W. G. Schroeder, English patent 25,404, 1905; German patents 163,372, 204,061, 204,062, 240,874; C. Petitpierre, French patent 353,753; E. Wörner, German patent 175,381; Th. Smith, United States patent 855,071; J. C. Shears, English patent 12,700, 1906; G. Bounet, German patent 168,714, 1906; Gaulin, English patents 18,249, 1902; 22,875, 1903; Talansier, United States patent 1,042,171; Berberich, French patent 451,028.

The solidified margarine is taken out of the cooling cisterns by means of long wooden spoons, placed in wooden waggons (where adhering water drains off), and is then carted to large kneading machines. These consist of huge, circular, wooden tables, which rotate slowly, whilst at the same time a set of conical, fluted, or specially shaped rollers move along the top of the revolving tables. The margarine is thus thoroughly worked through, and the excess of water squeezed out, so that a homogeneous mass results. This is then salted[3] to taste, mixed with a little colouring matter (if permitted by law[4]), and again submitted to thorough kneading, in order to produce the required texture throughout the whole mass. At this stage also other additions (such as sugar, perfumes, etc., see p. 37) are made. The margarine is finally moulded into lumps, pats, rolls, or any other desired shape.[5]

A general working recipe for the manufacture of margarine containing oleomargarine as a preponderant basis is as follows :—Mix 65 parts of oleomargarine, 20 parts of vegetable oils, and 30 parts of milk. The yield is 100 parts of finished product, 15 parts of water being eliminated in the course of manufacture. The more milk used, the better will be the flavour of the margarine. A mixture of oleo oil, neutral lard and cotton seed together with albumin, milk sugar, and soluble salts obtained by churning the fat mixture with sterilised whey has been patented by *Filbert.*[6]

For still lower qualities maize oil is said to be used in the United States, but owing to the very pronounced flavour this oil possesses it can only be employed for the lowest brands of margarine, as it is extremely difficult to remove or to mask the peculiar grainy flavour of maize oil. Lard is not used so extensively in Europe as in the United States. In this country oleomargarine is prepared exclusively from beef fat. Mutton fat, which imparts an unpleasant ("animal") flavour to the margarine, is, however, used in continental margarine factories. In Russia sunflower oil is used in the manufacture of margarine, and mixtures of this oil with coconut oil, butter, and oleomargarine are even fraudulently substituted for genuine butter. The use of soya bean oil has also been proposed.[1] During the last few years the proportion of oleomargarine has been reduced partly for the reason that the supply of it has become too restricted to fill the demand.

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[1] German patents 204,061, 204,062.

[2] English patent 4623, 1909.

[3] In Holland and in Germany 3 per cent of salt is generally added. The lowest grades of margarine usually contain the highest amount of salt. The salt is required as a preservative, especially in the margarines made with sour milk.

[4] According to Article 2 of the French Law of 15th April 1897, it is forbidden to colour margarine. In the United States also it is illegal to add colouring matters.

[5] Mallinson, English patent 28,077, 1911; Downs, English patent 9393, 1911.

[6] United States patent 995,777.

Margarines made exclusively from vegetable fats and oils usually consist of a basis of coconut or palm kernel oil.

The object of the margarine maker being to render his product as closely similar to butter as possible, and to take away the "tallowy" or too strongly "oily" taste of the material, some manufacturers (provided the law permits) add butter. Others add small quantities of volatile acids or their glycerides,[2] volatile aldehydes,[3] mixed glycerides containing butyric acid,[4] such as dibutyromonostearin and dicaprylomonostearin,[5] or "butter perfumes" which consist chiefly of volatile acids, such as propionic, butyric, caproic. Also coumarin (sold as an emulsion with sesamé oil), oil of bananas,[6] would fall under the head of "perfumes." Flavouring material produced by the action of bacteria on caseïn and lactose has been patented by *Wilson.*[7] The use of proteins extracted from leguminous plants has been patented by *De Bruyn.*[8]

It should, however, be stated that margarines prepared from the best materials in an unobjectionable manner do not require any of these additions. The latter are chiefly used in order to mask low grade materials or for fraudulent purposes so as to produce in the hands of the analyst a fictitious *Reichert-Meissl* value. Hence the so-called "improvers," which are sold as secret preparations, are unnecessary. The incorporation of ozonised air during the kneading process which is said to give an improved flavour to the margarine has been patented by *Svendsen.*[9]

An important point is to produce margarine which will froth and "brown" on heating, so that even in cooking the margarine may resemble butter. Since the property of butter to brown and froth is due to caseïn and milk sugar, it is evident that the more milk used in the manufacture of margarine, the nearer will the product approximate to butter.

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[1] Korentschewski and Zimmermann, *Chem. Zeit.*, 1905, 777.

[2] English patent 15,535, 1898 (Wohlgemuth); English patents 15,649, 22,458, 1900; French patent 279,497; United States patent 1,004,891.

[3] German patent 135,081 (Neudörfer and Klimont); French patent 308,153.

[4] Possible addition of tributyrin discussed by H. Fincke (x.), *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xvi. 666.

[5] German patents 102,539, 107,870.

[6] H. A. Snelling, English patent 8279, 1908.

[7] English patent 24,050, 1911.

[8] English patent 119,052, 1917.

[9] Norwegian patent 19,107, 1909.

Milk is largely used in this country and in America; but in some continental countries (see below) where the law forbids the addition of more than a strictly limited quantity of milk, a number of patents have been taken out[1] for substances which are credited with imparting to margarine the desired properties. Prominent amongst these patented products are caseïn and other albuminoids.[2] Some patentees claim cholesterol and cholesteryl esters,[3] or lecithin.[4]

Fendler[5] has shown that 0·5 per cent of egg yolk (or 0·05 per cent of lecithin) imparts to the margarine the property of "frothing," but not that of "browning." In order to produce the latter as well, an addition of sugar must be made. Egg yolk being cheaper than lecithin, it is, of course, more economical to add the former.[6]

Vegetable waxes have also been proposed as admixtures, and the use of beeswax[7] for this purpose has even been patented, although the addition of such substances must seriously interfere with the digestibility of the margarine.

Besides the taste, the consistence also plays an important part in the valuation of margarine. If the finished margarine has not been properly cooled, or has not been worked sufficiently on the tables, its consistence may be either too "greasy" or too "sandy," *i.e.* the semi-crystalline mass has not been properly "broken," and its grain differs from that of a properly prepared dairy butter. Some margarines are also finally mixed with a little glycerin, or glucose, or sugar, in order to improve the texture or to give them a glossy appearance and also a sweeter taste. Sulphur dioxide has been detected in margarine containing glucose.[8]

The addition of glucose, which has been patented by *Schmitt*,[9] or cane sugar must, however, be considered a mistake, as this only leads to premature development of fungi on the margarine.[10]

The manufacture of butter substitutes is differently affected by legislation in different countries.[11] In this country the adding of butter to margarine in any proportion was at first allowed, for, according to the Margarine Act of 1887, any " butter " containing even the smallest quantity of foreign fat was looked upon as margarine. By the Margarine Clause of the Foods and Drugs Act, 1899, however, the maximum proportion of butter fat in margarine has been restricted to 10 per cent.

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[1] Cp. German patent 112,687, 113,382, 116,792. (The last-named patent has been cancelled.)

[2] Under the name "Vitello," a mixture of egg yolk and glucose has been patented (Bernegau, German patent 97,057), and has been largely used in Holland. This patent has recently been declared invalid. Cp. also German patent 113,382 (Evers), and English patent 21,626, 1900 (Neisse and Bolle); E. V. Bühler, English patent 6417, 1901; R. Jurgens, English patent 8099, 1903; D. Müller, English patent 12,916, 1906; S. Mitscherlich, English patent 9015, 1907; Dr. Riegel's Nahrungsmittel-Werke, French patent 378,281; A. Bernstein, German patent 183,689, 1906; J. H. Boll, German patent 173,112; H. Mohr, German patent 170,163; Riegel, English patent 12,095, 1907 (cp. footnote, p. 117); P. A. Schmitt, French patent 460,614.

[3] Sprinz, English patent 7620, 1901; German patent 127,376.

[4] German patent 142,397; Reeser Margarine Fabrik, and C. Fresenius.

[5] *Chem. Revue*, 1904, 123.

[6] Cp. J. Müller, German patent 221,698.

[7] English patent 22,905, 1900; German patent 124,410; French patent 302,125, 316,986. Cp. also J. Müller, German patent 221,698.

[8] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1911, xxiv. 742.

[9] English patent 27,487, 1911.

[10] Cp. Zoffmann, *Chem. Revue*, 1904, 7; 1911, 4.

[11] A. Lavalle, *Die Margarine Gesetzgebung*, Bremen, 1896; *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, 1904. *Report from the Select Committee on Butter Trade*, London, 1906.

This restriction has been confirmed by the " Butter and Margarine Act of 1907," and it has been further enacted that margarine must not contain more than 16 per cent of water. Margarine factories must be registered, and are open to Government inspection. Prohibited preservatives must not be used, nor is an excess of boric acid allowed (see " Butter," Vol. II. p. 802). According to the same Act " margarine " means " any article of food, whether mixed with butter or not, which resembles butter and is not milk-blended butter."

It may be noted here that in Canada, for margarine intended for home consumption, the addition of sodium benzoate up to 1 part in 1000 and of salicylic acid up to 1 part in 5000 is permitted. Cp. " Butter Fat," Vol. II. p. 804.

In the United States the mixing of butter with margarine is not forbidden, provided this product be sold as " oleomargarine," but the artificial colouring of margarine is forbidden.—In France, up to the promulgation of the Law of 15th April 1897, the admixture of butter with margarine was permitted, provided the article so prepared was sold with a proper declaration as to its composition. Since then the maximum amount of butter that may be admixed with margarine has been fixed at 10 per cent. This amount, which includes the butter fat, is introduced with the milk in the course of manufacture.—In Germany, (Law of 15/6/1897), as also in Austria (Law of 25/10/1901), the mixing of margarine with butter is prohibited, both in the course of manufacture and as an addition to the finished margarine. Since in the manufacture of margarine no more than 100 parts of milk or a corresponding quantity of cream may be used for 100 parts of fat, the German and Austrian margarines may not contain more than 3·5 per cent of butter fat in the margarine fat; hence the *Reichert-Meissl* values of the German and Austrian margarines must not exceed the figure 2 (provided coconut and palm nut oils have not been used, for in that event the *Reichert-Meissl* value will be higher; see below). By an Imperial Statute it is made obligatory that the margarine manufactures in Germany add at least 10 parts of sesamé oil for every 100 parts of fats and oils used. This is done in order to facilitate the detection of margarine in butter (earlier proposals to add a " latent " colouring matter, such as phenolphthalein or dimethylamidoazobenzene, having been rejected). It has however, been shown in Vol. II. " Butterfat," p. 867, that the sesamé oil test is not infallible.

In Austria also the addition of 10 per cent of sesamé oil has been made obligatory.—In Belgium the margarine manufacturer is bound, according to the Law of 4th May 1900, to use at least 5 parts of sesamé oil in 100 parts of fatty matter, and 0·2 part of dry potato starch.—In Denmark the proportion of butter fat allowed in margarine has been reduced from 50 per cent to 15 per cent, and it is forbidden to produce and deal in margarine which has a deeper yellow tint than a certain officially fixed one. The margarine (margarine fat ?) must contain at least 10 per cent of sesamé oil (Law of 1st January 1906). According to the Dutch "Butter Act," margarine must not be sold which has a higher *Reichert-Wollny* value than 10.[1]

The German Government had rejected the proposal to use potato starch for "earmarking" margarine, on the ground, it is stated, that starch is too easily removed by washing the margarine with water. This objection would, however, not hold good, since *Mainsbrecq*[2] has shown that if the starch is dried and then mixed with fat, it cannot be washed out with water, the fat forming, as it were, a protecting layer. The advantage of starch as an earmarking substance consists not only in that it is a cheap substance which does not in any way influence the quality of the margarine, but furthermore in that its presence can be detected by two independent methods, namely, by the iodine test and by microscopical examination, so that even if a colouring matter should be discovered which would give a blue coloration with iodine solution, the microscopical examination could still be relied upon. This becomes all the more important since the "earmarking" by sesamé oil has been rendered nugatory by the employment of—legally permitted—colouring matters, which give with hydrochloric acid a similar coloration to that produced in the *Baudouin* reaction for sesamé oil. These colouring matters so tenaciously adhere to the fat substance (being more readily soluble in it than in dilute hydrochloric acid) that an inordinately large number—20 to 30 and more—of washings with hydrochloric acid must be carried out before the colouring matter is removed. The chromogenetic substance in sesamé oil is at the same time destroyed, so that the presence of sesamé oil can no longer be thus detected.[3] *Arnold*[4] decolorises the colouring matter by means of stannous chloride, which is stated not to impair the delicacy of the *Baudouin* test. *Arnold* operates as follows: The fat dissolved in petroleum ether is shaken with hydrochloric acid containing a little stannous chloride, and warmed for a short time in the water bath. When the red coloration has disappeared the furfurol solution is added in the usual manner. The evidence which the author has given in this respect before the Parliamentary Committee has, amongst other reasons, induced the Committee not to recommend sesamé oil as an earmarking substance for margarine.[5]

The methods of examining margarine ("oleomargarine"), and especially of distinguishing it from true butter fat, have been exhaustively dealt with in the preceding chapter, under "Butter Fat."

A reliable preliminary test for discriminating between margarine not containing added butter, and genuine butter fat, is to heat the isolated fat with a small quantity of alcoholic potash, insufficient to effect complete saponification. In the presence of butter fat ethyl butyrate, readily recognised by its pleasant smell recalling that of pine-apples, is formed. A number of margarines examined by the author failed to give the odour of the butyrate. On adding, however, a small quantity of genuine butter, the characteristic smell was immediately observed. It would therefore appear that the small quantity of butter fat which is introduced into margarine with the milk is not readily revealed by this test. It must also be borne in mind that butyric esters may have been added to the margarine.

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, xvii. 679.

[2] *Bull. de l'Assoc. Belge*, 1889 (12), 185.

[3] Cp. Fendler, *Chem. Revue*, 1905, 10.

[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1913, xxvi. 655.

[5] For other objections against the employment of sesamé oil in the manufacture of margarine, compare *Report from the Select Committee on Butter Trade*, London, 1906.

In order to determine quantitatively the amount of butter fat in margarine, especially with a view to testing whether it exceeds the legal limit of 10 per cent, the *Reichert-Wollny* method has been agreed upon as the official test[1] by the Government Laboratory and a Committee of the Council of the Society of Public Analysts. The following table gives the amount of butter fat which was assumed to be present in a margarine (in the absence of coconut and palm nut oils[2]) in case the following *Reichert-Wollny* numbers have been found :—

Reichert-Wollny Number of the Margarine Fat.	Percentage of Butter Fat assumed to be present in the Margarine Fat.
4·0	10
4·3	11
4·6	12
4·9	13
5·2	14
5·5	15
5·9	16
6·2	17
6·5	18
6·8	19
7·1	20

Since, however, margarines are now being prepared which contain as much as 30-40 per cent of coconut or palm nut oil, the indications furnished by the *Reichert-Wollny* value alone are not sufficient to raise the presumption that the margarine contains more butter fat than is permitted under the Foods and Drugs Act.

In cases of this kind the high saponification number of the margarine fat would in the first instance reveal the presence of coconut or palm nut oil. *J. Reilly and W. J. Hickinbottom*[3] determine the relative volatility of the acids obtained in the *Reichert* distillation process by distilling them in a current of steam, and base thereon a method for differentiating butter fat from the fats of the coconut oil group. The figures they publish, however, lie too close together to admit of the determination of small amounts of butter fat in mixtures.

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[1] *Analyst*, 1900, 309 (see Vol. I. Chap. VI.).

[2] It may be pointed out in this connection that Bemelmans (*Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiii. 492) found in the Reichert-Meissl distillate of a margarine fat benzoic acid (added as a preservative), which, of course, increased the Reichert-Wollny number. To a smaller extent the same effect would be produced by salicylic acid (cp. Vol. II. p. 804).

[3] *Sci. Proc. Royal Dublin Soc.*, 1920, 16, 131.

If the quantity of coconut oil be small, then the determination of the saponification value alone cannot lead to decisive results. In that event the determination of the insoluble volatile acids (by the methods of *Müntz and Coudon* or of *Polenske*, Vol. II. Chap. XIV. p. 844) would furnish further indications.[1] If even then unmistakable results are not obtained, the margarine fat may be resolved by extraction with alcohol into two portions, viz. a somewhat more easily soluble portion and an insoluble portion. Coconut oil, being much more soluble in alcohol than the usual constituents of margarine (oleomargarine, lard, cotton seed oil, etc.), would pass into the alcoholic solution to a greater extent than do the other fats and oils, and the residue after distilling off the alcohol can then be examined with advantage by determining the saponification value, *Reichert-Meissl* value, and the titration number of the insoluble volatile fatty acids (see below). With regard to the detection of coconut oil, cp. also *Hinks*' microscopical method, Vol. II. p. 857.

The problem becomes more difficult if it is required to determine the amounts of butter fat and of coconut oil (or palm kernel oil), if present conjointly, in a margarine. *A. Kirschner*[2] endeavoured to solve it by basing himself on a principle first suggested by *K. Jensen*,[3] viz. to determine the amount of caprylic acid in the aqueous solution obtained in the *Reichert* distillation process.

In the case of butter fat this solution contains preponderantly butyric acid—which has not been found in coconut oil or in palm nut oil—and also caprylic acid, which latter occurs in butter fat to a small extent only, whereas in the case of coconut oil a comparatively considerable amount of caprylic acid will be obtained. The silver salt of butyric acid is easily soluble in water, whereas caprylic acid yields a silver salt which is only sparingly soluble in this menstruum.

Kirschner's method consists in saponifying 5 grms. of margarine fat in the usual manner, and determining the *Reichert-Meissl* value. To 100 c.c. of the distillate 0·5 grm. of silver sulphate is added, the solution is well shaken and allowed to stand one hour, so that the precipitate may settle out. The precipitate is filtered off through a dry filter, the filtrate is acidified with dilute sulphuric acid and distilled again. The distillate is titrated with decinormal alkali and yields a "new number," which is a measure of those volatile acids, the silver salts of which are soluble in a neutral solution. By determining this same number and also the *Reichert-Meissl* values in (1) a margarine fat free from coconut oil, (2) the same margarine fat mixed with 10 per cent of coconut oil, and (3) margarine fat No. 1 mixed with 10 per cent of butter fat, an equation can be formed which allows to calculate the percentage of butter fat in a margarine fat containing coconut oil, after the *Reichert-Meissl* value and the " new number " of the margarine fat have been determined. *Kirschner* derives the following equation :—

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[1] Although these strictures have been pointed out in the third edition of this work (1904) it was only late in 1909 that a paragraph was added as follows: "The limiting figure of 4 obtained by the Reichert-Wollny method described and the table of figures connected therewith are not applicable to those cases of margarine in which the insoluble acids number exceeds 1" (*Analyst*, 1909, 514).

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, ix. 65; cp. also Arnold, *ibid.*, 1907, xiv. 172.

[3] *Farmaceutisk Titende*, 1903, 385.

Per cent of butter fat = 4·319 × " new number " − 0·456 × Reichert-Meissl value − 2·15.

Although check experiments made by *Kirschner* with mixtures of margarine fat with coconut oil and butter fat yielded very good results, the objection must be raised that for the derivation of the above equation only three series of values had been used. Furthermore, in view of the varying composition of butter fat (see Chap. XV. " Butter Fat "), and in view of the minutiæ of detail of manipulation which must be observed in order to obtain comparable results, this method, although involving the application of a very useful principle, must be accepted with reserve. *Revis and Bolton*[1] point out that although this method shows little superiority over *Polenske's* method for the detection of coconut oil in butter, it has great value in the analysis of margarine containing coconut oil and (or) butter.

The relationship between the *Reichert-Meissl* value, the *Polenske* value, and the *Kirschner* value has been the subject of a large amount of work for which the original papers given in the footnote[2] should be consulted.

Blichfeldt[3] determines the amounts of the acids whose silver salts are soluble and insoluble in a solution of sodium nitrate. The distillation is conducted in a special apparatus, for the details of which the original paper should be consulted.[4] The following figures have been found by this method :—

	Total Volatile Acids c.c. $\frac{N}{10}$ KOH.	Soluble Silver Salts.	Insoluble Silver Salts.
Butter fat . .	32	29	3
Coconut oil . .	20	4	16
Palm kernel oil .	15	3	12

Useful indications as to the nature of the fat under examination may be derived by determining the melting point of the fatty acids liberated from the insoluble silver salts, those from coconut oil ranging from 8 to 10° C. and from palm kernel oil from 21 to 24° C.[5] This may also be done with the fatty acids liberated from the sodium salts obtained in the *Polenske* process.

The author, however, found that the soluble silver salts in coconut oil were 1·16 only.

G. Van B. Gilmour[6] proceeds as in *Blichfeldt's* method using the same apparatus. Instead, however, of precipitating the volatile acids with silver nitrate they are liberated by the addition of an amount of $\frac{n}{10}$ sulphuric acid sufficient exactly to neutralise the $\frac{n}{10}$ alkali used for titration. The solution is saturated with sodium chloride and filtered, the filtrate containing acids soluble in saturated brine being titrated. The following numbers have been recorded for pure fats :—

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[1] *Analyst*, 1911, 334.

[2] Bolton and Revis, *Analyst*, 1912, 183; Cranfield, *ibid.*, 1915, 439; Richmond, *ibid.*, 1919, 166.

[3] *Journ. Soc. Chem. Ind.*, 1910, 792.

[4] *Ibid.*, 1919, 150 T.

[5] M. Pettersen, *ibid.*, 1919, 150 T.

[6] *Analyst*, 1920, 2.

	Butter Fat.	Coconut Oil.	Palm Kernel Oil.
Total volatile acids . . .	26·0-33·0	19·5-22·5	12·0-14·0
Soluble acids	20·0-23·5	1·3-1·8	1·0-1·3
Insoluble acids. . . .	5·0-9·5	18·0-20·7	11·0-12·7

Cassal and Gerrans [1] saponify 3 grms. of fat, decompose the soap with 10 c.c. hydrochloric acid, and add 50 grms. of anhydrous calcium chloride. This mixture is then distilled in a current of steam from a calcium chloride bath kept at 141-146° C., until 500 c.c. have passed over. The insoluble volatile acids are filtered off, washed with cold water, and dissolved in hot alcohol. They are then titrated with $\frac{n}{10}$ alkali. These observers find as the average number yielded by pure butter fat 16, and that yielded by coconut oil 66.

Another method, which would seem to promise more reliable results, has been proposed for this purpose by *Arnold*,[2] viz. to treat the margarine fat with alcohol, and to examine the alcohol-soluble portion, which would then contain the more soluble portions of both coconut oil and butter fat. *Settimj and Maurantonio* [3] state that the greater proportion of the vegetable oils present in a margarine may be removed by heating 150 c.c. of the fat with 200 c.c. of 95 per cent alcohol, with continuous shaking. The mixture is allowed to cool and the alcoholic layer decanted. The determination of the saponification value, of the *Reichert-Meissl* value, of the titration number of the insoluble volatile acids, of the mean molecular weights of the soluble volatile acids, and also of the insoluble volatile acids, would then furnish such data as may lead to an approximate determination of butter fat and coconut oil in margarine fat. The tables containing *Arnold's* values as given in Chapter XIV. under "Lard," pp. 711, "Beef Fat," p. 777, "Butter Fat," pp. 823 and 856, in conjunction with the following tables, will materially assist in interpreting the results :—

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[1] *Chem. News*, 1910, 190.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 1129, 1178; *ibid.*, 1911, xxi. 589; *ibid.*, 1914, xxvii. 379.

[3] *Ann. Lab. Chim. d. Gabelle*, 1912, (6) 203.

	Butyro-refractometer at 40° C. "Degrees"	Saponification Value.	Reichert-Meissl Value.	Mean Molecular Weight of the Soluble Volatile Acids.	c.c. $\frac{1}{10}$ KOH required for Insoluble Volatile Acids (Polenske's method).	Iodine Value.	Non-volatile Fatty Acids.			Yielded Alcohol-soluble portion. Grms.
							Butyro-refractometer at 40° C. "Degrees"	Neutralisation Value.	Iodine Value.	
Margarine containing 4 per cent of Butter Fat										
I. Original Fat	48·7	197·1	1·95	...	0·55 [1]	55·3	...	...	...	...
II. Alcohol-soluble Fat	51·5	200·05	6·80	102·3	0·90 [1]	71·8	...	...	...	8·2
III. Alcohol-insoluble Fat	...	...	...	...	...	...	...	...	...	...
Margarine containing 5 per cent of Butter Fat										
I. Original Fat	48·2	201·0	2·10	104·5	0·55 [1]	49·3	33·9	209·5	50·7	...
II. Alcohol-soluble Fat	52·9	207·0	6·60	102·4	0·90 [1]	56·6	38·0	211·1	57·9	9·7
III. Alcohol-insoluble Fat	48·2	200·5	1·60	...	0·55 [1]	47·5	33·2	207·6	49·3	...
Beef Fat containing 5 per cent of Butter Fat										
I. Original Fat	46·5	201·3	2·26	104·1	0·70 [1]	39·0	...	...	...	...
II. Alcohol-soluble Fat	46·9	205·6	9·10	105·5	0·95 [1]	50·3	...	...	...	7·4
Margarine containing 2 per cent of Coconut Oil										
I. Original Fat	47·3	201·0	1·30	...	0·65	49·5	33·1	210·5	51·2	...
II. Alcohol-soluble Fat	50·0	207·5	3·95	...	1·75 [1]	54·1	36·4	214·9	55·9	9·8
III. Alcohol-insoluble Fat	48·2	201·7	0·93	...	0·55	48·4	33·2	207·9	49·1	...

---

[1] The acids are solid.

	Butyro-refractometer at 40° C. "Degrees"	Saponification Value.	Reichert-Meissl Value.	Mean Molecular Weight of the Soluble Volatile Acids.	c.c. $\frac{1}{10}$ KOH required for Insoluble Volatile Acids (Polenske's method).	Iodine Value.	Non-volatile Fatty Acids.			Yielded Alcohol-soluble portion. Grms.
							Butyro-refractometer at 40° C. "Degrees"	Neutralisation Value.	Iodine Value.	
Margarine containing 8 per cent of Coconut Oil										
I. Original Fat	45·2	203·4	2·30	140·0	1·15	35·2	...	...	...	...
II. Alcohol-soluble Fat	42·7	226·8	7·48	135·7	6·35 [1]	32·2	...	...	...	8·5
III. Alcohol-insoluble Fat	45·7	202·1	1·80	...	0·90	34·9	...	...	...	...
Margarine containing 2 per cent of Coconut Oil and 5 per cent of Butter Fat										
I. Original Fat	47·5	201·2	2·04	...	0·70 [1]	45·9	...	...	...	...
II. Alcohol-soluble Fat	51·4	210·0	9·13	111·6	2·35 [2]	53·6	...	...	...	9·9
III. Alcohol-insoluble Fat	47·4	199·4	1·35	...	0·65 [1]	44·6	...	...	...	...
Margarine containing 5 per cent of Coconut Oil and 5 per cent of Butter Fat										
I. Original Fat	47·1	201·6	2·92	118·0	0·85 [1]	44·9	...	...	...	...
II. Alcohol-soluble Fat	46·3	220·7	11·61	117·6	4·25 [2]	49·0	...	...	...	10·5
III. Alcohol-insoluble Fat	47·2	200·5	2·20	122·0	0·66 [1]	44·7	...	...	...	...
Margarine containing 6 per cent of Coconut Oil and 4 per cent of Butter Fat										
I. Original Fat	46·9	202·2	2·81	126·8	0·90 [1]	44·7	...	...	...	...
II. Alcohol-soluble Fat	45·4	221·8	10·67	123·7	5·15 [2]	46·6	...	...	...	10·5
III. Alcohol-insoluble Fat	46·9	201·6	2·15	128·0	0·80 [1]	44·3	...	...	...	...

---

[1] The acids are solid.

[2] The acids are liquid.

The following table due to *Monhaupt* shows the relationship between the *Reichert-Meissl* values, titration number of the insoluble volatile acids, and *Kirschner's* method for margarines containing varying amount of coconut oil and butter fat.

Mixtures of Fat containing Coconut Oil and Butter Fat

Coconut Oil.	Butter Fat.	Reichert-Meissl Value.	c.c. $\frac{1}{10}$ KOH required for Insoluble Volatile Acids (Polenske's Method).	New Number (Kirschner's Method).
Per cent.	Per cent.			
10	0	1·76	1·10	0·30
	1	1·95	1·10	0·48
	2	2·26	1·15	0·69
15	0	2·31	1·52	0·34
	1	2·52	1·60	0·55
	2	2·81	1·60	0·76
20	0	3·74	2·00	0·50
	1	4·00	2·05	0·81
	2	4·18	2·10	0·98
25	0	3·85	2·65	0·61
	1	4·10	2·80	0·84
	2	4·35	2·85	1·02
30	0	4·07	3·10	0·64
	1	4·74	3·30	0·88
	2	4·84	3·25	1·15
35	0	4·95	4·15	0·73
	1	5·22	4·30	0·96
	2	5·50	4·20	1·23

In conclusion the author adds a few analyses of margarines, which indicate the course of examination to be adopted. This embraces the determination of water (which in this country must not exceed 16 per cent), ash, total fat, and examination of fat (if desired).

[TABLE

Analyses of some Margarines free from Coconut Oil

	Water.	Fat.	Solids Not Fat.	Ash.	NaCl.	Saponification Value.	Iodine Value.	Reichert Value.	Insoluble Volatile Acids.	Insoluble Acids + Unsaponifiable.	Butyro-refractometer. At 45° C.	Observer.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.		Per cent.	"Degrees."	
Margarine 1	8·8	88·78	2·33	1·58	1·53	...	...	0·33	...	94·5	...	Partheil [2]
,, 2	8·5	88·81	2·69	1·6	1·74	...	...	0·44	...	94	43·2	,,
,, 3	8·6	88·9	2·4	1·6	1·5	...	...	1·43	...	94·7	...	,,
,, 4	...	...	...	...	...	193·70	...	2·07	...	...	...	Beythien and Strauss [3]
,, 5	...	...	...	...	...	194·00	53·60	1·44	...	96·30	...	
,, 6	...	...	...	...	...	200·60	...	1·78	...	...	...	,,
,, 7	...	...	...	...	...	203·75	...	1·93	...	...	...	,,
,, 8	...	...	...	...	...	195·00	60·90	2·40	...	95·88	...	,,
,, 9	...	...	...	...	...	196·05	...	1·19	...	...	...	,,
,, 10	...	...	...	...	...	199·80	52·12	1·52	...	95·50	...	,,
,, 11	12·9	...	4·04	1·71	1·5	193·7	...	1·2	0·67	...	...	Strunk
,, 12	12·9	...	4·41	1·59	...	190·1	...	1·19	-0·59	...	...	,,

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[1] *Apoth. Zeit.*, 12, 220.

[2] *Zeits. f. Unters. d. Nahrys- u. Genussm.*, 1902, 856.

A method due to *Shrewsbury and Knapp*[1] based on the property of lauric acid (which constitutes a large proportion of the fatty acids of coconut oil) of being soluble in dilute alcohol is carried out as follows:—5 grms. of fat are saponified by the *Leffmann-Beam* process, and the soap diluted in a separating funnel with 200 c.c. of boiling water. 5 c.c. of sulphuric acid (prepared by mixing 100 c.c. of concentrated sulphuric acid with 400 c.c. distilled water) are added, and the mixture shaken for one minute. After standing for five minutes the aqueous solution is run off and separated as far as possible from the fatty acids. The fatty acids remaining in the separating funnel are dissolved in 50 c.c. of 90 per cent (by weight) alcohol, and put into a flask. 36 c.c. of cold water are run into the separator and the alcoholic solution boiled and poured into the water. The mixture is run into the flask and then back into the separator. The separating funnel is shaken for 30 seconds and allowed to stand for three minutes in order to permit the insoluble fatty acids to separate. 70 c.c. of the clear alcoholic solution are measured off and titrated with tenth normal alkali. The mean amount of alkali required for English butters is given as 27·7, with a maximum of 32, and that of lard and coconut oil 15·7 and 163 respectively.

The examination of a large number of samples of English and foreign butters by *Ross, Race, and Maudsley*[2] points, however, to the maximum figure being about 35·5. The figures for coconut stearine and cacao butter are 138·5 and 16·5. This method has been critically examined by *G. D. Elsdon and C. R. Bagshawe*,[3] who have introduced some slight modifications with a view to obtaining more concordant results.

Elsdon[4] also uses this method in conjunction with the number obtained by *Polenske's* process for calculating the respective amounts of coconut and palm kernel oils.

Cribb and Richards[5] calculate the proportion of coconut oil to butter fat in a margarine by the aid of the relationship between the *Reichert-Meissl* and the *Polenske* figures. The proportion of coconut oil is arrived at as follows:—From the alkali required for the insoluble volatile acids, one-tenth of the *Reichert-Meissl* value is deducted, the remainder being calculated to coconut oil on the assumption that the mean titration number for the insoluble volatile acids of coconut oil is 17·5. The proportion of butter is found by subtracting from the *Reichert-Meissl* value the alkali required by the volatile acids of the coconut oil, the proportion of which has been found above, assuming that the *Reichert-Meissl* value of coconut oil is about 6·5. These observers also make a correction for the solubility of the so-called insoluble volatile acids, but having regard to the enormous variations in the natural products this appears to be a somewhat needless refinement. For this reason also too much reliance should not be placed on the results obtained by these calculations, for, whereas it is a comparatively easy matter to calculate the proportions in a mixture of fats whose analytical values are known, it is a very much more difficult problem when the origin of the components is unknown.

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[1] *Analyst*, 1910, 385.

[2] *Ibid.*, 1911, 195.

[3] *Ibid.*, 1917, 72.

[4] *Ibid.*, 1917, 298.

[5] *Ibid.*, 1911, 327; cp. also Arnaud and Hawley, *Analyst*, 1912, 122.

The examination of a few specimens of margarine fat, containing coconut oil, gave the following numbers :—

Margarine Fats containing Coconut Oil

Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Insoluble Volatile Acids.	Insoluble Acids and Unsaponifiable.	Observer.
216·34	49·46	5·50	...	92·97	Beythien and Strauss
220·35	49·06	4·50	...	93·04	
217·45	...	4·50	...	...	"
210·12	...	4·10	...	...	"
218·24	49·25	4·60	...	92·98	"
237·7	...	5·3	8·9	...	Strunk
248·7	...	5·6	11·3	...	"

F. H. Trim[1] bases a method for the estimation of coconut oil, palm kernel oil, and arachis oil on the correlation between the refractive index and the melting point. It should be noted the figures given refer to oils that are practically neutral.

The following determined figures are taken as the standard :—

Oil.	Refractive Index at 40° C.	Melting Point. ° C.
Coconut oil	1·44897	24·85
Palm kernel oil . . .	1·45097	28·35
Arachis oil	1·46235	− 8

This method may prove useful in works where quick analytical control is needed. Graphs are given in the original paper for calculating the components of mixtures containing all three oils.

W. N. Stokoe[2] differentiates coconut and palm kernel oils by determining the temperature at which the insoluble volatile acids obtained in the determination of the *Polenske* value begin to crystallise.

The following numbers have been recorded for mixtures of the two oils ; cp. also page 43.

Coconut Oil. Per cent.	Palm Kernel Oil. Per cent.	"Seeding" Point. ° C.
100	0	10·75
85	15	11·8
75	25	13·4
60	40	15·5
50	50	16·9
40	60	17·9
25	75	19·5
10	90	21·8
0	100	22·75

[1] *Journ. Soc. Chem. Ind.*, 1920, 307 T.

[2] *Ibid.*, 1921, 57 T.

For a method for detecting coconut oil in butter fat by the determination of the miscibility curves, the original paper should be consulted.[1]

The detection of the individual oils and fats in margarine is carried out in the manner described under "Butter Fat" and by following the course indicated in Chap. XI. In an examination of this kind, the determination of stearic acid may lead to valuable indications, as is evidenced by the following numbers published by *Hehner and Mitchell* :—

Fat.	Containing Stearic Acid. Per cent.
Oleomargarine . . .	21·3-23·6
Margarine I. . . .	24·8
„ II. . . .	11·72

Butter fat contains less than 1 per cent of stearic acid ; cp., however, Vol. I. Chap. VIII.

Leffmann and also *Geisler*[2] stated that they found in American "oleomargarines" from 9·72 to 11·5 per cent of paraffin wax;[3] hence the quantitative determination of the unsaponifiable matter should not be omitted. With regard to the examination for boric acid and other preservatives (salicylic, benzoic acids) and colouring matter, cp. Chap. XIV. under "Butter Fat." *Arnold*[4] gives the following test for a yellow dye which is used as a margarine colour :—2 c.c. of the melted fat are dissolved in 4 c.c. of petroleum ether, and the solution shaken with 1 c.c. of hydrochloric acid of specific gravity 1·19. The lower acid layer will be coloured yellow to orange and may be decolorised by the addition of one drop of stannous chloride solution. A method for the detection of egg-yolk has been worked out by *Fendler*.[5]

In the examination of the aqueous layer obtained on melting the sample of margarine, an alkaline reaction may also be caused by the presence of ammonium carbonate, which some makers add to their margarine.[6]

In the following table the estimated production of margarine in the most important countries during the year 1912 is given :—[7]

Country.	Actual Production (estimated).	Imports, 1912.	Exports, 1912.
	Kilogrammes.	Kilogrammes.	Kilogrammes.
United Kingdom	...	80,000,000	...
United States of America . .	70,900,000	...	...
Germany	192,000,000	...	...
Denmark	39,000,000	2,000,000	...
Sweden	22,000,000	147,829	22,171
Norway	20,000,000	...	...
Austria-Hungary	1500 waggons	...	...

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[1] Louise, *Ann. d. falsific.*, 1911, 302.

[2] *Journ. Amer. Chem. Soc.*, 1899 (21), 605.

[3] In this connection it may be mentioned that even the admixture of 60 per cent of refined mineral oil to edible fats with a view to producing a "compound edible fat" has been patented (English patent 9526, 1894).

[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1913, 654.

[5] *Ber. d. Deutsch Pharm. Ges.*, 1903, 284.

[6] K. Fisher and Grunert, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1904, viii. 414.

[7] *Census Bulletin.*

The imports of margarine during the last twenty-two years into the United Kingdom are stated in the following table :—

Year.	Cwts.
1899	958,586
1900	924,034
1901	965,546
1902	958,211
1903	876,446
1904	950,368
1905	1,105,374
1906	1,111,099
1907	885,068
1908	813,447
1909	868,292
1910	1,120,812
1911	944,405
1912	1,352,427
1913	1,518,297
1914	1,529,219
1915	2,052,183
1916	2,752,866
1917	1,807,806
1918	301,650
1919	459,369
1920	897,972

The home production of margarine is increasing from year to year, and may now be estimated to exceed 1,000,000 cwts. per annum. Reliable statistical data are, however, not available.

The following table shows the kinds and quantities of materials used in the production of " oleomargarine " in the United States :—

Materials.	Pounds, 1899.	Percentage, 1899.	Percentage, 1912.
Neutral lard	31,297,251	34·27	16·27
"Oleo oil"	24,491,769	26·82	34·29
Cotton seed oil	4,357,514	4·77	14·36
Sesamé oil	486,310	0·53	0·28
Colouring matter	148,970	0·16	0·21
Sugar	110,164	0·12	0·06
Glycerin	8,963	0·01	...
"Stearine"	5,890	0·007	0·76
Glucose	2,550	0·003	0·05
Milk	14,200,576	15·55	20·09
Salt	6,772,670	7·42	7·33
"Butter oil"[1]	4,342,904	4·76	...
Butter	1,568,319	1·72	2·98
Cream	3,527,410	3·86	3·09
Total	91,322,260	100·00	99·77

The quantities of " oleomargarine " produced in the United States of America during the years 1897 to 1920 have been stated officially as follows :—

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[1] This is a special brand of cotton seed oil (see Vol. II. Chap. XIV.).

State.	1897.	1898.	1899.	1900.	1901.	1902.	1903.	1904.	1913.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Connecticut	5,086,884	5,290,412	5,690,437	7,982,578	8,154,385	10,997,240	7,026,383	5,420,268	12,592,686
Illinois	24,747,971	20,835,316	38,685,490	46,334,358	41,610,286	49,359,177	30,495,955	20,729,107	87,384,185
Indiana	1,313,835	5,485,631	7,125,215	10,704,181	9,222,351	11,192,496	7,028,342	2,608,715	1,390,500
Kansas	5,533,257	13,331,614	13,231,382	16,483,147	16,360,484	19,793,666	14,044,666	9,471,920	12,812,241
Kentucky	...	247,640	1,060,064	2,203,721	162,289	311,753	101,292	...	...
Maryland	381,900	988,268	1,866,750	4,100,100	2,683,055	6,132,116	225,056	349,644	369,400
Missouri	220,510	409,705	514,182	712,377	3,996,395	76,710	319,121	360,391	2,691,278
New Jersey	5,234,997	8,795,891	12,321,008	15,197,296	459,006	911,871	541,720	964,166	8,617,262
Ohio	...	...	...	...	16,436,961	21,244,118	9,242,065	6,933,211	16,322,061
Pennsylvania	...	...	...	...	2,142,330	2,522,736	1,482,521	502,870	...
Texas	...	...	...	...	414,000	550,900	624,490	717,932	1,348,797
Other States	5,205	4,250	1,100	545,893	4,791	41,070	105,827	113,626	1,599,792
Total	42,534,559	55,388,727	80,495,628	104,263,651	101,646,333	123,133,853	71,237,438	48,071,850	145,227,862

State.	1914.	1915.	1916.	1917.	1918.	1919.	1920.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Connecticut	...	...	...	...	1,111	...	2,166,648
Illinois	89,220,748	100,379,921	100,526,176	146,656,041	196,610,328	188,733,866	187,276,640
Indiana	1,079,210	1,009,060	1,079,225	1,979,146	1,730,302	1,945,855	1,199,400
Kansas	11,630,683	8,545,803	8,570,342	13,098,752	18,892,740	20,699,310	21,255,990
Kentucky	...	22	199	4,157	...	...	...
Maryland	359,190	311,790	307,455	485,498	1,009,288	1,471,561	2,230,984
Missouri	2,781,641	4,143,206	5,264,820	6,795,890	9,516,094	11,615,258	19,301,395
New Jersey	6,335,650	8,152,176	9,733,080	20,207,340	35,166,534	43,842,008	49,060,917
Ohio	15,645,908	14,127,979	14,884,154	23,666,099	30,473,358	28,445,409	32,775,594
Pennsylvania	...	...	...	...	14,451	...	...
Texas	1,050,540	872,000	667,800	1,572,000	2,799,400	3,025,260	2,070,800
Other States	13,660,035	5,726,773	9,490,474	18,178,253	40,032,204	49,197,398	64,226,354
Total	141,763,605	143,268,730	150,523,725	232,643,176	336,345,810	348,975,925	381,564,722

The amount of margarine (" oleomargarine," " imitation butter ") exported from the United States in lbs. and the value in dollars are given in the following table :—[1]

Year.	Lbs.	Dollars.	Year.	Lbs.	Dollars.
1896	6,063,699	587,269	1909	2,889,058	293,635
1897	4,864,351	472,856	1910	3,418,632	349,972
1898	4,328,536	386,297	1911	3,794,939	408,459
1899	5,549,322	509,703	1912	3,627,425	372,567
1900	4,256,067	416,544	1913	2,967,582	311,485
1901	4,990,699	484,501	1914	2,532,821	263,453
1902	5,721,254	601,521	1915	5,252,183	617,035
1903	7,645,652	798,273	1916	5,426,221	640,480
1904	6,137,251	605,874	1917	5,651,267	901,659
1905	7,863,164	711,038	1918	6,309,896	1,631,267
1906	11,794,174	1,033,256	1919	22,939,589	6,576,760
1907	5,397,609	520,406	1920	16,557,746	4,567,120
1908	2,938,175	299,746	1921	3,329,049	672,327

As will be seen, the production of margarine in the United States has fallen off considerably in consequence of recent legislation injuriously affecting the production and sale of margarine. The same effect has been produced in Germany by the Margarine Act of 1902, and the production has fallen from 123,133,853 lbs. in the fiscal year 1901-2 to 72,484,761 lbs. in 1902-3 and 48,071,850 lbs. in 1903-4. In 1912, however, the production had risen to 385,805,000 lbs. The production of margarine in Denmark may be gathered from the following figures :—

Year.	Lbs.	Year.	Lbs.
1892–93	16,312,844	1916	1,242,560
1899–1900	32,530,911	1917	730,620
1905–6	53,490,000	1918	25,300
1906–7	57,850,000	1919	872,080
1911	77,880,000	1920	1,221,450

It may be added that the manufacture and sale of margarine is forbidden in Canada, hence all the " oleo oil " produced there is exported.

Under the name of " margarine " may be also comprised emulsions of fat with water without the addition of milk.

Some of these emulsions, consisting of oleomargarine—oleo oil—or lard, or mixtures of the two, emulsified with about 16 per cent of water, have been sold especially as butter adulterants. The analyses of some of these have been given under " Butter Fat," Vol. II. Chap. XIV. p. 826. The fraudulent use for which these " margarines " are intended naturally restricts their sale.

Another kind of fat emulsion, consisting of vegetable butters emulsified with water, or with milk and egg yolk, etc., more properly belongs to the " Vegetable Butters " (see below), although legislation in different countries may demand its being sold under the laws affecting margarine.

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[1] From 1919 calendar year.

(β) Vegetable Butters

French—*Beurres végétaux.* German—*Vegetabilische Buttersorten.* Italian—*Burri vegetabili.*

Under the heading "Vegetable Butters" all those fats or mixtures of fats are included which are exclusively of vegetable origin, and have at the ordinary temperature a consistence approaching that of butter or lard. Their origin differentiates them from the products named under the heading "Suet Substitutes" (p. 30).

A fat corresponding to this description is "cotton seed stearine"; indeed, the cotton seed stearine obtained from the best qualities of cotton seed oil, fit for consumption, is specially prepared and sold as a butter substitute in those countries where the inhabitants are forbidden by their religious tenets to consume beef fat or hog fat (India, Turkey). In commerce such vegetable butters are known as "vegaline," "cottolene," etc. The manufacturing processes for producing cotton seed stearine have been described in the preceding chapter (Vol. II. Chap. XIV.).

Coconut oil and palm kernel oil lend themselves to the same purposes, especially in temperate climates, provided they are refined so as to offer no objection on account of taste and odour. The great demand that had arisen during the last three decades for butter substitutes, a demand that could not be fully met by margarine alone on account of the limited supplies of beef fat, directed the attention, in the first instance, to the problem of refining coconut oil so as to render it fit for edible purposes. The earliest experiments made in this direction appear to date from the year 1880. In the year 1882 *Jeserich and Meinert-Bünau* patented a process of refining coconut and palm kernel oils. This process consisted in deodorising the oils by a current of high pressure steam (6 to 8 atmospheres), and removing, by means of magnesia, the free fatty acids still left in the fats after steaming. This process seems to have been carried out on a manufacturing scale at first in Germany, but the product was still tainted with a peculiar flavour, which was at that time believed to be caused exclusively by the free fatty acids of coconut oil, but which has been shown by *Haller and Lassieur* to be due to the natural presence of methylheptylketone and methylnonylketone in coconut oil.

Attempts were then made on a large scale to remove by treatment with alcohol [1] the free fatty acids and, at the same time, the odorous substances. On account of the costliness of the process, and for other obvious reasons, this method also had been abandoned. Yet the alcohol process appears to have been again attempted on a large scale.[2]

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[1] Purification by means of alcohol was first used by Chevreul, and appears to have been proposed as a working process first by Démachy in the beginning of the last century (cp. German patent 19,819).

[2] French patent 361,966 (Urbain and Feige). Cp. also French patent 394,456 (Welfling); French patent 394,530 (G. van der Heyden).

At first most of the products were sold (secretly) as butter adulterants, but in the same degree as the detection of even small quantities of coconut oil in butter fat was rendered easy by the application of searching analytical methods, and as more elaborate processes of refining were invented, coconut oil butter won for itself—under its proper name—an independent position as a butter substitute, and began to find extensive use in confectionery and as a culinary fat. The fat is at present mostly sold under fancy names, the number of which has grown exceedingly extensive of late years.[1] These are prepared from the best brands of coconut oil (Cochin), either imported as such or in the form of well-dried copra of best quality.[2] Some vegetable butters are made from expressed palm kernel oil.

According to *Kreis*[3] artificial nut butters are being manufactured consisting of 80 per cent of coconut oil and 20 per cent of ground walnuts.

The refining processes proper, embracing chiefly the removal of the free fatty acids, and the deodorisation of the oil are guarded as valuable secrets, both as regards the details of the process and the apparatus employed. Moreover, the processes in use differ considerably, as is evidenced by the different qualities of the various commercial coconut (and palm kernel) oil butters in respect of taste and odour. Hence the reader can only be referred to the general indications given on p. 25, and, for further details, to the patent specifications mentioned above.

The difficulties experienced in the conversion of coconut oil into vegetable butter were frequently attributed to the presence of proteins. *Freundlich*[4] has shown that the proportion of proteins in a number of coconut oils was *nil*, or at most amounted to 0·18 per cent, and he therefore rejects as untenable the view that proteins are the cause of the difficulties. Since, however, *Freundlich* found in the emulsified layers, which are formed between oil and washwaters in the course of the manufacturing process, substances which, after removing the fat with ether, would appear from their proportions of nitrogen to contain from 0·08 to 2·85 per cent of proteins, the question must still be left an open one. In the author's opinion it appears likely that *Raschig's* chloramine reaction may prove of assistance in deciding this question.

Haller and Lassieur have, however, shown that the difficulties are due to the extremely great trouble involved in the total removal of the volatile ketones.

The free fatty acids of the raw material are recovered as a by-product in the form of alkaline salts (soda soap) or salts of alkaline earth (lime soap, magnesia soap). These soaps occlude a considerable amount of neutral fat, up to 40 and even 60 per cent of their total weight. The soapy mass is usually decomposed with mineral acid and boiled until a clear layer floats on the top. The fatty layer, consisting of free fatty acids and neutral fat, has become a commercial article, and is sold as soap stock (see Chap. XVI.) under the name of "acid oil."

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[1] Cp. also Fendler, *Chem. Revue,* 1906, Nos. 10, 11, 12.

[2] G. C. Warr, United States patent 992,525.

[3] *Chem. Revue,* 1912, 196.

[4] *Chem. Revue,* 1907, 302; 1908, 3.

The difficulty which coconut oil offered, in that it became, on solidification, too hard to be used like butter, has been overcome by passing the finished product between rollers in a kind of milling or kneading machine, whereby a " soft texture " is imparted to the coconut oil, so that it can be spread like butter [1] (" Kneaded Coconut Butter "). In order to prevent the partial melting of the coconut oil in the kneading machine, *Schlinck* [2] uses quickly rotating knife blades which shred the fat in thin slices from solidified blocks of suitable size.

The commercial success which attended the introduction of some of the best brands of vegetable butters prepared from coconut and palm kernel oils has acted as an incentive for increased production, so that in the year 1902, in Europe alone, about 10,000 tons of edible coconut oil and palm nut oil butters were manufactured. In the year 1907 the European production was estimated to have amounted to no less than 50,000 to 60,000 tons. Reliable figures for the European production are not available to-day, but the annual amount probably lies in the neighbourhood of a quarter of a million tons.

The manufacture of vegetable butters occupies an important place in this country, as also in France, Germany, and Austria. It is also being extended in Switzerland, Belgium, and Holland.

In the United States also, considerable quantities of copra and coconut oil are worked up for vegetable butter, especially since the export of raw material from the Philippines has been largely diverted to the United States.

Vegetable butter from coconut oil is brought into commerce, not only in its original white colour, but also coloured yellow in order to render it more like margarine in appearance. The description and analysis of a number of such coconut butters has been given by *Fendler*. In the endeavour to make these products still more similar to butter (or margarine), some manufacturers actually produce emulsions of coconut oil with water and salt, egg-yolk and salt, or even milk, egg-yolk, and salt—in other words, produce a margarine (see p. 37).[3] In some countries these products undoubtedly fall under the definition of margarine, especially when they contain small quantities of oils other than coconut oil (*e.g.* cotton seed oil) [4]; hence in those countries they must contain the amount of sesamé oil prescribed for margarine. The analyses of a number of such emulsified coconut butters have been published by *Fendler*.[5] They would be most suitably termed " vegetable margarines."

The examination of these products embraces the determination of free fatty acids and ash. Further analytical tests refer to the solidifying point of the fat, the titer test of the fatty acids, and the determination of unsaponifiable matter. The last-named test has acquired some importance, as during recent years paraffin wax and heavy paraffin oil have been frequently added to edible coconut oil with a view to imparting to it a butter-like consistence. *Arnold*[1] found in a vegetable butter 3·9 per cent of unsaponifiable matter, which consisted of a yellow viscous liquid of the iodine value 2·65, saponification value 0, and showing in the butyro-refractometer 74·4 " degrees " at 40° C.

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[1] Cp. also G. Müller, French patent 334,366. A curious patent for rendering vegetable butter " capable of being spread " claims the addition of 7 to 8 per cent of alcohol (P. Kolesch, English patent 18,499, 1907); United States patent 910,827; German patent 208,147. Full specification given, *Chem. Revue*, 1909, 287.

[2] German patent 193,045. Cp. also French patent 373,996, and first addition No. 7751 (P. D. Massimi).

[3] Cp. also English patent 12,355, 1907 (A. M. Sörensen), which claims the addition of salt, sugar, and egg-yolk.

[4] Cp. Rigaut, French patent 398,241.

[5] *Chem. Revue*, 1906, Nos. 10, 11, 12.

In judging a sample the chief importance must be given to the taste of the product, and its odour on warming. The detailed examination and identification of the fatty matter is carried out according to the methods described in earlier chapters.

Besides coconut oil and palm kernel oil, other tropical vegetable fats, such as margosa oil, mowrah seed oil, and shea butter, lend themselves to the manufacture of vegetable butters, and since the time the author[2] has proposed these, such products have been manufactured on a large scale and placed on the market. They were at first used to a large extent as adulterants of butter fat, instead of as substitutes, but with the increased demand for edible fats, they are used as such or for compounding in the industry of margarine, or of vegetable butters.

The " vegetable butters " furnish the raw material for the production of " chocolate fats " (see below).

(3) LARD SUBSTITUTES

French—*Succédanés du saindoux*; *Saindoux artificiels.* German—*Kunstspeisefett*; *Kunstschmalz.* Italian—*Strutti artificiali.*

The commercial lard substitutes consist chiefly of a mixture of lard, or " lard stearine," with " beef stearine "[3] (" oleostearine "), cotton seed stearine, cotton seed oil, maize oil, arachis oil, sesamé oil, coconut oil, and palm kernel oil. In the infancy of this industry these artificial products were sold under such names as " refined lard," " commercial lard " (cp. Vol. II. p. 716). Other products (*e.g.* " lard compound ") contain no lard whatever, being judiciously prepared mixtures of beef stearine and cotton seed oil,[4] such as described above under (*a*). At present, however, all lard substitutes proper contain lard, or at least " lard stearine," as a basis. The United States Government Meat Inspection Service has issued a regulation providing that a substance composed of lard and oleostearine or other animal fat and vegetable oil may be labelled " lard compound," but in such cases the names of all the ingredients must be shown upon the label and in all cases the proportion of lard must be equal to, or greater than, that of the other combined ingredients. The manufacture consists simply in mixing the various fats and oils in the melted state in a mixing machine, and cooling the mixture rapidly by running it over cooling cylinders (cp. "Lard"), so as to destroy any tendency to crystallisation. The proportions of the several ingredients are varied, not only according to the state of the market values, but also according to the seasons. In summer the quantity of the harder fats is increased, whereas in winter the proportion of the more fluid constituents becomes higher. Thus it is feasible to place on the market a product of the same consistence all the year round. When mixing together the various ingredients without the aid of "lard coolers," care must be taken that the mixture is run out of the mixing machine at the proper temperature so as to prevent separation.

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xv. 280.

[2] Lewkowitsch, Cantor Lectures : " Oils and Fats : their Uses and Applications," 1904.

[3] On the Continent mutton stearine is used also.

[4] United States patent 980,809.

In order to impart to the finished mixture a pure white colour, it is usual to stir air into the fat until it acquires a salvelike consistence. The stirring with air must not, however, be carried too far, as otherwise the lard substitute not only becomes more liable to rancidity but also acquires a foamy consistence.

In some German works lard substitutes are finally treated with onions and condiments, so to as impart to the product the taste of a cooking fat. They are frequently sold under the name "Bratenfett" ("culinary fat," "dripping").

The examination of these substitutes is carried out on the lines fully indicated under "Lard" (Vol. II. Chap. XIV. p. 699).

The quantitative determination of the constituent fats of a given lard substitute is a difficult problem, which cannot always be solved satisfactorily.

The proportion of cotton seed oil can be calculated approximately from the iodine value of the liquid fatty acids of the sample and the iodine values of the liquid fatty acids of lard and cotton seed oil. For the last two products mean values must be assumed. *Wesson and Lane*,[1] basing themselves on a series of experiments, proposed for the approximate calculation of the cotton seed oil in a lard substitute, the following formula :—

$$\frac{a-b}{c-b} \times \frac{j}{k} = x,$$

where

a = Iodine value of liquid fatty acids in the sample.
b = Iodine value of liquid fatty acids of lard.
c = Iodine value of liquid fatty acids of cotton seed oil.
j = Per cent of liquid fatty acids found.
k = Per cent of liquid fatty acids in cotton seed oil.
x = Per cent of cotton seed oil.

The results are stated to be nearly correct if the separation of the solid from the liquid fatty acids is effected with petroleum ether. If ethylether be employed the results are said to be from 3 to 5 per cent too low. *Wesson and Lane* propose to determine the amount of oleostearine by subjecting the sample to *Wesson's cooling test*. The principle of this test rests on the observation that a mixture of oleostearine and cotton seed oil of known titer test crystallises at a much higher temperature than does pure lard of the same titer, and on the further observation that a mixture of lard oil and lard stearine crystallises at a much lower temperature than does a mixture of the same amount of lard oil with oleostearine. The approximate amount of oleostearine in a given lard substitute may therefore be derived by observing the manner of its crystallisation side by side with that of a known mixture, in an apparatus fitted up as follows: A piece of wood about eight inches square and half an inch thick is pierced with eight holes, in which (up to) seven test tubes and a thermometer are inserted. This board is laid on the top of a 600 c.c. beaker. The beaker itself is fitted into a thin piece of board, which in its turn is laid on the top of a wider beaker, holding about 2000 c.c.

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[1] *Journ. Soc. Chem. Ind.*, 1905, 714.

After the amount of cotton seed oil has been ascertained with the help of the above given formula, the titer test of the sample is determined in the manner directed by Circular No. 22 of the United States Department of Agriculture (see Vol. I. Chap. VIII.), and the approximate amount of oleostearine (the average titer of which is taken as 50° C.) in it, x is calculated with the aid of the following formula :—

$$a - b' - \frac{3700 - 37b}{100} = 0{\cdot}13x,$$

where

a = Titer test of the sample.
b = The percentage of cotton seed oil found.
$b' = \frac{33 \times b}{100}$. The figure 33 is the average titer of cotton seed oil and 37 the average titer of lard.

Thus, in a given sample, the amount of cotton seed oil was found to be 40 per cent and the titer test 38° C., whence the proportion of oleostearine was calculated as 20 per cent.

A number of standard mixtures are then made up, one containing the amount of cotton seed oil, oleostearine, and lard as calculated, the others 5 and 2·5 per cent above and below the amount of oleostearine indicated by the last formula. The standards and the original sample are carefully dried and filtered (as moisture or solid particles of dust seriously interfere with the results). The test-tubes are half filled with the samples and kept at the same temperature in a beaker filled with hot water. The 600 c.c. beaker is then filled with boiled out distilled water, and allowed to cool to about 40° C., according to the melting point of the sample. The test-tubes are next corked, put through the holes of the board, and placed on the 600 c.c. beaker, so that the lower ends are at a distance of about half an inch from the bottom of the beaker. The thermometer is so inserted that its bulb is in the lower half of the water. The 600 c.c. beaker is then placed in the 2000 c.c beaker, and the apparatus allowed to cool. When the oleostearine commences to separate in the sample, it is compared with that standard test-tube which most closely approximates it in appearance. Thus the amount of oleostearine present in the sample is arrived at with some accuracy. The first indications of crystallisation are generally correct, but must not be as decisive, for with the further fall of the temperature another standard might yield a more correct figure. The authors of this method state that the results are accurate to about 2 per cent, and that 3 per cent to 5 per cent of oleostearine in a lard substitute can be easily detected.

The examination of the unsaponifiable matter should not be omitted, since patents have even been taken out for lard substitutes containing mineral oils.

The extent which the lard substitutes industry has reached may be gathered from the following table, in which the amounts of lard substitutes and lard compounds (cottolene, lardine, etc.) exported from the United States are given :—

Year.	Lbs.	Dollars.	Year.	Lbs.	Dollars.
1896	1,709,923	102,279	1909	75,183,196	6,115,307
1897	16,261,991	857,708	1910	74,556,603	6,887,738
1898	21,343,028	1,118,659	1911	73,754,400	7,070,967
1899	22,144,717	1,200,231	1912	62,522,888	5,183,689
1900	25,852,685	1,475,064	1913	67,456,832	5,915,759
1901	23,359,966	1,559,878	1914	58,303,564	5,489,139
1902	36,201,744	2,687,653	1915	69,980,614	6,045,752
1903	46,130,004	3,607,542	1916	52,843,311	5,147,434
1904	53,603,545	3,581,813	1917	56,359,493	8,269,844
1905	61,215,187	3,613,235	1918	31,278,382	6,633,640
1906	67,621,310	4,154,183	1919	124,962,950	31,605,885
1907	80,148,861	6,166,910	1920	32,051,458	7,218,845
1908	75,183,210	6,035,418	1921	48,206,583	5,548,931

(4) CACAO BUTTER SUBSTITUTES—CHOCOLATE FATS

French—*Succédanés du beurre cacao*; *Graisses de chocolat.*
German—*Kakaobutter Surrogate*; *Schokoladenfette.*

The natural chocolate fat is cacao butter (Vol. II. p. 591).

The best chocolates were formerly made from the comminuted cacao bean mass by the addition of sugar, etc. Thus the whole of the natural fat was left in the mixture. Lower kinds of chocolate were obtained by expressing the mass, leaving only about 30 per cent or even 10 per cent or 12 per cent of cacao butter, and replacing the removed cacao butter by cheaper fats. Since a demand for " fondants " and " pralinées " has arisen, the amount of fat naturally present in cacao beans no longer suffices for the satisfactory manufacture of these products, and a further amount of fat is required. This is furnished by those works which prepare cacao powder, or have a surplus of cacao butter from the manufacture of low-class chocolates. A greatly increased demand for cacao butter has also arisen since it was found that for each part of cacao fat added to the mass, six parts of flour could be admixed without altering the appearance of the finished chocolate.

Cacao butter being one of the most expensive fats, a demand for cheap substitutes has arisen. Animal fats are, as a rule, unsuitable for chocolate manufacture, for, unless they are refined carefully, they are apt to impart an unpleasant flavour ("animal flavour") to the chocolate. Hence chocolate fat substitutes are mostly prepared from vegetable fats.

The chocolate fat substitutes in vogue at present are obtained from coconut oil or palm kernel oil, refined as described under (β) "Vegetable Butters." The original oils being too "soft," *i.e.* having too low a melting point, the "stearines" from coconut oil and palm kernel oil are prepared by melting the refined coconut oil and palm kernel oil, and allowing to cool down to a suitable temperature so that the glycerides of the solid fatty acids crystallise out. The partly solidified mass is then expressed in hydraulic presses (much in the same fashion as "premier jus" is obtained) to remove the coconut or palm kernel "oleine." According to the length of time during which the crystallised mass is allowed to stand under pressure, and according to the pressure and temperature employed, the melting point of the coconut or palm kernel stearine varies.

The ethereal extract from a chocolate containing coconut oil has a different appearance after drying in a current of air to that obtained from a chocolate containing its own natural fat. *Wauters*[1] states that 10 per cent of coconut oil may thus be detected.

In the following table the results of an examination of a number of substitutes are given (cp. also the physical and chemical characteristics tabulated, Vol. II. p. 652) :—

Cacao Butter Substitutes (Lewkowitsch)

No.	Acid Value.	Saponification Value.	Iodine Value.	Melting Point (Closed Capillary Tube).	Reichert-Meissl Value.	Insoluble Volatile.
				°C.		
1	0·43	250·81	...	28·3–28·5	3·52	...
2	1·63	236·52	...	28·3–28·85	4·03	...
3	0·392	250·21	...	27·7	4·20	...
4	0·971	249·01	...	31·6	4·89	...
5	0·825	233·46	...	31·62	3·48	...
6	0·55	247·99	...	27·75	3·24	...
7	...	254·3	6·6	25	6·34	...
8	...	...	...	28·6	3·63	...
9	0·311	244·4	8·40	26·6	7·48	...
10	0·484	241·9	9·67	27·2	8·1	...
11	...	...	...	29·4–30·2 (31·6 over mercury)	...	...
12	0·248	...	...	...	...	...
13	0·236	...	...	...	...	...
14	0·19	...	...	...	...	...
15	1·34	...	...	...	...	...
16	1·52	...	...	...	...	...
17	1·44	...	...	...	...	...
18	0·51	257·4	...	28·31	5·88	11·59
19	0·56	250·5	...	31·34	5·51	10·20
20	0·64	252·0	...	30·33	5·32	11·32
21	...	...	...	...	...	...
22	...	...	...	...	...	...
23	...	...	...	...	...	...

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[1] *VII. Inter. Cong. App. Chem*, 1909, Sec. viii. 194.

Cacao Butter Substitutes (*Bontoux*)

No.	Acid Value.	Saponification Value.	Iodine Value.	Melting Point (Closed Capillary Tube).	Reichert-Meissl Value.
1	0·5	255–258	4·2–5·2	29·2	3·40–3·82
2	0·5	250–252·3	5·0–6·2	31·8	2·33–2·50
3	0·6	252·2–252·5	8·3	32·0	2·48
4	0·7	252·9	10·5	29·2	4·80
5	0·7	248·4–251·8	15·2	27·5	6·0
6	0·7	242·5	3·8–5·0	32·2	2·0–2·1
7	1·1	193·1	31·9–32·3	36·9	0·95
8	1·2	199·4	35·5–36·7	36·5	2·10–2·29

Since the melting points of the commercial coconut "stearines" (sold under fancy names, such as "cacaoline," "cocoline," etc.) are still somewhat too low for the purposes of the chocolate manufacturer, they in their turn are being "stiffened," *i.e.* adulterated, with small quantities of animal fats. It has even been stated that Japan wax[1] has been admixed to raise the melting point. Mineral waxes, like paraffin wax, and ceresin, should be considered as inadmissible adulterants, as they are indigestible, although as much as 8·4 per cent of paraffin wax has been found by the author in commercial specimens.

In the analysis of chocolate the determination of the amount of milk products has become of importance (milk chocolate, cream chocolate). The presence of butter will be shown in the absence of coconut oil by the *Reichert-Meissl* value. If coconut oil is present the phytosteryl acetate test will give the readiest answer. For the determination of the casein *Baier*[2] gives the following method: 10 grms. of the fat-free chocolate are mixed with 200 c.c. of a 1 per cent solution of sodium oxalate in a 250 c.c. measuring flask. The mixture is boiled and allowed to stand overnight, the flask is then filled up to 250 c.c. and the contents filtered. 100 c.c. of the filtrate are mixed with 5 c.c. of a 5 per cent solution of uranium acetate and 30 per cent acetic acid added, drop by drop, until a precipitate results. The precipitate is separated off in a centrifugal and washed with a solution containing 5 per cent uranium acetate and 3 per cent of 30 per cent acetic acid until free from sodium oxalate. The nitrogen in this is determined by *Kjeldahl's* method and calculated to casein.

In the following table some analyses of milk chocolates are given[3]:—

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[1] Possetto, *Giorn. Farm. Chim.*, 1901 (51), 337.

[2] *Zeits. f. angew. Chem.*, 1909, 1335; cp. also Dubois, *United States Dept. of Agric. Bureau of Chem.*, 1913 (162), 130.

[3] Booth, Crib, and Richards, *Analyst*, 1909, 146.

[TABLE

	English (10 Samples).			Swiss, German, Austrian, and Belgian (10 Samples).		
	Min.	Max.	Mean.	Min.	Max.	Mean.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total fat	23·7	36·0	31·8	29·2	33·4	30·8
Made up of—						
Milk fat	2·6	8·3	5·5	5·8	13·6	8·1
Cacao butter	21·0	31·6	26·3	15·6	23·8	22·7
Milk sugar	3·8	11·1	8·04	5·2	11·0	8·26
Cane or beet sugar	32·4	54·3	43·2	35·0	52·7	42·6
Nitrogen	0·76	1·68	1·18	1·10	1·30	1·24

Sachs[1] states that dika fat, Borneo tallow, and illipé oil are used as chocolate fats, either alone or in admixture with coconut and palm nut stearines.[2]

The examination of these products embraces the determination of the melting point, detection of unsaponifiable matter, and of animal fats.

For the examination of the fat used in the manufacture of a given chocolate, the latter may be extracted with ether or with petroleum ether (cp. Vol. II. p. 597). *A. Kreutz*[3] proposes the extraction of chocolate with solid chloral-alcoholate (cp. also *Bordas and Touplain*[4]). For the analytical examination of chocolate (which necessarily falls outside the scope of this work) cp. *Booth, Cribb, and Richards.*[5]

Under the heading of edible oils and fats would also seem to fall those oils and fats, or preparations containing them to a preponderant extent, that are used for **medicinal purposes.** They can only be noticed very briefly in this work :—

1. **Effervescent Oils.**—(See p. 29).

2. **Phosphorised Oils.** — (French—*Huiles phosphorées.* German—*Phosphoröle.*)—These oils are prepared by dissolving dry phosphorus in edible oils in the absence of air. The quantity of dissolved phosphorus is about 1 per cent (cp. Vol. I. Chap. IV.). The most suitable oil for the manufacture of phosphorised oil is said to be almond oil ;[6] the oxidation of the phosphorus is said to be best prevented by the addition of 1 per cent of limonene.[7]

3. **Castor Oil Preparations.** — In order to render castor oil less distasteful when taken internally, preparations are put on the market,

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[1] *Chem. Revue,* 1908, 9; cp. also C. Grimme, *Gordian,* 1914, 19, 6971.

[2] Cp. Lewkowitsch, Cantor Lectures : "Oils and Fats : their Uses and Applications," 1904.

[3] *Zeits. f. Unters. d. Nahrgs- u. Genussm.,* 1908, xv. 680 ; xvi. 585.

[4] *Ann. des falsif.,* 1908, 12.

[5] *Analyst,* 1909, 134.

[6] Korte, *Pharm. Zeit.,* 1908, 53,655. With regard to the keeping properties of phosphorised cod liver oil, cp. Heiduschka, *Archiv f. Kinderheilkunde,* 1906 (33), 1 ; Schweissinger, *Pharm. Zentralh.,* 1909, 75.

[7] Bohrisch, *Pharm. Zentralh.,* 1909, 597.

made by evaporating a mixture of castor oil with milk until a dry powder is obtained (*Winternitz*[1]), or by mixing salts of caseïn and milk sugar with castor oil.[2]

With the same object in view, namely, to convert castor oil into the form of a dry powder, emulsions of this oil with gum arabic are mixed with magnesia powder[3] and lecithin.

Allophanester of castor oil $C_3H_5O_3(CO\cdot C_{17}H_{32}O\cdot C_2O_2N_2H_3)_3$ is obtained by boiling a solution of castor oil in benzene with hydrochloride of urea. It forms a white powder, melting point 61°-62° C.[4]

4. **Cod Liver Oil Preparation.**—In order to render cod liver oil more palatable it is emulsified[5] with solutions of gum arabic, sugar, etc., to which are added the hypophosphites of soda, potash, and lime and also lecithin (cp. also p. 29) or malt extract.

II.—BURNING OILS. ILLUMINATING OILS

French—*Huiles d'éclairage*; *Huiles à brûler.* German—*Brennöle, Leuchtöle.* Italian—*Olii da lumi.*

In the earliest stages of the history of the human race animal fats were used as illuminants. No doubt the first torches were made with the aid of blubber oils, bear fat, deer fat, etc. The employment of vegetable oils for illuminating purposes must have constituted an important progress, as not only receptacles for the oil but also wicks (made from the pith of rushes) had to be invented. In semi-civilised countries every kind of oil or fat that was obtainable locally would thus have been pressed into the service of man, and it must be ascribed to this circumstance that even at present in these countries fatty oils and fats are used as burning oils to the exclusion of mineral oils. Thus even butter fat serves to-day as a burning oil in the Hindu temples of Southern India (where cow *ghi* only may be used) and in the lamaseries of Tibet.

Up to the middle of the last century fatty oils (olive oil and rape oil) were the illuminants throughout Europe; even at present linseed oil and castor oil are largely used as burning oils in India, as is tung oil in Japan.

Although the development of the mineral oil industry has caused a great reduction in the amount of fatty oils used for illumination, nevertheless their employment is still considerable. Thus enormous quantities of rape oil are used on the railways in this country, as is lard oil in the United States and olive oil in Italy. The best brands of seal oil and whale oil are employed as illuminants in lighthouses. Whale oil in Norway serves largely for lighting the streets.

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[1] German patent 150,554.

[2] German patent 152,596.

[3] May, *Journ. Soc. Chem. Ind.*, 1909, 826.

[4] German patent 211,197, *Vereinigte Chimin. fabrik*, Zimmer and Co.

[5] Sheard, English patent 492, 1908; Hamburg, English patent 29,481, 1912; Kawai and Miwa, English patent 15,403, 1912; Weiss, English patent 418, 1910; Borthroyd and Wooliscroft, English patent 4623, 1909.

The technical preparation of these oils has been described in the foregoing chapter. Their examination comprises tests for purity and the determination of free fatty acids. The former include the detection of mucilaginous substances and of other impurities, such as mineral substances (ash), the presence of which is due to faulty refining. The impurities rise with the oil in the wick and are apt to clog it up, so that carbon is deposited, and the flame becomes smoky.

The determination of the free fatty acids is important, as oils containing more than 5 per cent of free fatty acids are unsuitable for burning, since they also cause charring of the wick and produce a smoky flame. As rape oil is usually refined with sulphuric acid, burning oils must be tested for mineral acids by shaking a somewhat large quantity of the oil with warm water and examining the aqueous solution (cp. Vol. I. Chap. IV. "Lubricating Oils").

Since drying oils and the semi-drying oils of the cotton seed oil group are unsuitable, their absence in a given burning oil must be ascertained by the methods given in the foregoing chapter.

The importance of these tests to large consumers may be gathered from the fact that lard oil adulterated with 25 per cent of cotton seed oil will not burn for longer than six to eight hours without clogging the wick, whereas pure lard oil will burn as long as twelve to fourteen hours.

The semi-drying oils belonging to the rape oil group occupy a prominent place amongst the burning oils in general use. The most important member of this group is rape oil (East Indian, German, French) itself. The best quality is represented by an expressed oil; extracted oil is less suitable. Jamba oil is distinctly inferior to the genuine rape seed oils, for although it may be considered a good burning oil, it does not burn as well as does "colza oil." Colza oil will burn for days without charring the wick, but Jamba oil clogs the threads much sooner. Jamba oil in its turn is superior as a burning oil to ravison oil, and therefore takes its place between ravison oil and best East Indian rape oil.

Of the non-drying oils olive oil was, and still is, extensively used in the Mediterranean countries, especially in Italy and Greece. No doubt to the latter country is due the custom of the Greek Orthodox Church to burn olive oil before the ikons. Olive oil for ritual purposes, "sanctuary oil," is now being fraudulently substituted in Russia by mixtures of coconut oil (35 parts), rape oil (5 parts), and mineral oil (65 parts of the specific gravity 0·86).

A large number of oils bearing fancy names, such as "signal oils," "weather oils," are mixtures of fatty oils with mineral oils. These are examined according to the methods described under the heading "Lubricating Oils."

III.—PAINT OILS

French—*Huiles siccatives*. German—*Maleröle*.

Under the term "paint oils" are comprised those vegetable oils which are used as vehicles for applying pigments to the surface of bodies, either as a preservative or for decorative purposes. Only the vegetable *drying* oils are useful; the paint oil *par excellence* is linseed oil. In the manufacture of high-class white paints for the use of artists, cold pressed walnut oil and poppy seed oil are employed in considerable quantities.[1] Tung oil, although a drying oil, is unsuitable for the manufacture of paints, as the skin which it forms on drying is soft and easily destroyed on exposure. It is, however, of value to the varnish maker. According to *Gardner*,[2] the best drier for use with tung oil is lead salt of the tung oil fatty acids fused with a small proportion of rosin and borate. The semi-drying oils, such as soya bean oil, cotton seed oil, and maize oil, are unsuitable as paint oils.

A comparison [3] of the rates of drying of some raw oils by exposing a film of oil on glass plates to a brisk current of air showed that linseed oil attained its maximum increase of weight after seven days. Chinese tung oil attained its maximum two days later, but gave an opaque film of frosted appearance. Fish oils reached their maximum increase in less than four days, but even after twenty days a skin had not formed.

The examination of these oils chiefly embraces tests for purity. The detection of adulterants, such as mineral oils, rosin oils,[4] and fish oils, has been fully described under the heading of linseed oil, etc. Fish oils, especially menhaden oil, were used in considerable quantities to adulterate linseed oil when the price of the latter was high, and a large number of linseed oil substitutes, consisting of linseed oil adulterated with fish oil, mineral oils, and rosin oils, were then placed on the market. Adulteration has, however, become much less frequent. Attempts have been made to convert heavy hydrocarbon oils into oils which will dry without leaving an oily residue by treating such heavy oils with steam at high temperatures.[5] The preparation of drying oils from fish oils by treatment with steam at high temperatures whereby the glycerides of the unsaturated fatty acids become polymerised has been patented by *Kampfe*.[6]

If the oil in a ready mixed paint has to be determined quantitatively, it must be separated from the pigment by extraction with ether (cp. p.156). The examination of the oil itself is carried out by the methods detailed in the foregoing chapters. In the manufacture of coloured pencils the use of blood serum as a binding agent has been patented.[7]

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[1] Cp. E. Täuber, *Chem. Zeit.*, 1909, 85, 94.

[2] *Journ. Franklin Inst.*, 1911, 55; *Eighth Int. Cong. Appl. Chem.*, 1912, Section V^e, 33.

[3] Redman, Weith and Brock, *Journ. Ind. and Eng. Chem.*, 1913, 630.

[4] French patent 398,813 (Silvestrini) protects an alcoholic solution of rosin oil.

[5] Greenstreet, French patent 446,475.

[6] English patent 15,012, 1912.

[7] Bössenroth, German patent 261,559.

In judging of the value of a drying oil for making paints, the effect of the pigment with which the oil is to be ground must not be lost sight of,[1] inasmuch as some pigments greatly facilitate the drying, whereas others retard it to such an extent that driers must necessarily be added.[2] A pigment consisting of the cyanamide of heavy metals, such as copper, has been advocated for the manufacture of paints suitable for preserving wood and iron.[3]

It should be noted that oils extracted by solvents are not suitable for the manufacture of high-class paints.

Since paints for common use are chiefly prepared with "boiled oils," the reader is referred for further information to the section on "Boiled Oils" (p. 142).

The consideration of the toxic properties of the vapours evolved by paints during the process of drying falls outside the scope of this work. The reader must, therefore, be referred to the original papers by *Gardner*[4] and by *French.*[5]

IV.—LUBRICATING OILS—LUBRICANTS

French—*Huiles lubrifiantes, huiles de graissage.* German—*Schmieröle, Schmiermittel.* Italian—*Olii lubrifianti.*

Before the advent of the industry of preparing lubricating oils from mineral oils, especially those from petroleum, the lubricating oils in use were almost exclusively represented by fatty oils, solid fats, and liquid waxes (see "Technology of Waxes," below). Hence the examination of lubricating oils formed a distinct province of fat analysis. Within the last decades the mineral oil industries have made such striking advances that their products have greatly restricted the employment of fatty oils for lubricating purposes and practically relegated these to a subsidiary position, inasmuch as they are chiefly used in admixture with mineral oils. Hence mineral oils, and mixtures of fatty oils with mineral oils, must be considered here briefly.

The solid lubricating greases also fall within the purview of fat analysis, and will therefore be dealt with at the end of this section.

Owing to the great technical importance of this subject, a number of works have been published, treating solely of lubricating oils and lubricants. Here only a concise survey of the subject can be given, and readers requiring special information must be referred to the works mentioned in the footnote.[6] The author subdivides the lubricants into four groups :—

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[1] Eibner, *Chem. Zeit.*, 1911, 753. Cp. also E. W. Boughton, *Journ. Soc. Chem. Ind.*, 1916, 852.

[2] Cp. Lotter, *Chem. Zeit.*, 1894, 1696.

[3] Falloni, German patent 263,622.

[4] *Oil and Colour Trades Journ.*, 1914, 1000, 2093; 1915, 673; C. A. Klein, *Journ. Ind. and Eng. Chem.*, 1915, 7, 99; and H. H. King, *ibid.*, 1915, 7, 502.

[5] *Ibid.*, 1914, 1818.

[6] Grossmann, *Die Schmiermittel*, Wiesbaden, 1909; Carpenter-Leask, *Soaps and Candles*, chap. xii. (written by J. Veitch Wilson); Holde, *Die Untersuchung der Schmiermittel*, Berlin, 1897; Archbutt and Deeley, *Lubrication and Lubricants*, London, 1900.

1. Fats (Fatty Oils and Solid Fats)—Liquid Waxes.
2. Mineral Oils.
3. Blended Oils (Mixtures of Groups (1) and (2)).
4. Greases, Solid Lubricants.

Strictly speaking, the "*wool oils*" belong to lubricating oils, but for practical reasons it is more convenient to consider them under a special heading (see below). It may be noted here that mineral oils or emulsions of a mineral oil with a solution of soap in water are used for oiling the inside of pottery moulds for the purpose of facilitating the removal of the moulded ware. Petroleum burning oil is also used for this purpose.

In a wider sense also aqueous emulsions of soap and oils used for purposes of lubrication (*e.g.* for cutting tools) belong to the lubricating oils. They will be dealt with more conveniently under the separate heading "Emulsified Oils" ("Emulsion Oils").

1. FATTY OILS AND SOLID FATS—LIQUID WAXES

The most important fatty oils used as lubricants are tallow oil, lard oil,[1] neat's foot oil, olive oil, rape oil, and castor oil. Tallow also is still largely employed. For delicate machinery hazel nut oil, porpoise oil, and dolphin oil (black fish oil) have come into vogue. Coconut oil is not suitable for lubrication.

The vegetable drying oils, the semi-drying oils belonging to the cotton seed oil group, fish oils, liver oils, and blubber oils (with the exception of porpoise and dolphin oils) are not suitable for lubricating purposes; hence their admixture with the above-named lubricating oils must be looked upon as adulteration.

The liquid waxes, sperm oil and Arctic sperm oil, which are fittingly considered here, are excellent lubricants, and are used almost exclusively for the lubrication of light machinery and of spindles.

The manufacturing and refining processes have been described under the heading of each oil, fat, and wax in the foregoing chapter, where also the methods of detecting adulterants will be found. The amount of unsaponifiable matter in the vegetable and animal lubricating oils should be small. The liquid waxes yield, of course, considerable quantities of alcohols, which are comprised in practice under the name "unsaponifiable matter."

2. MINERAL OILS

The mineral oils used for lubricating purposes are chiefly derived from crude petroleum, shale, and lignite. They are represented by hydrocarbons (saturated,[1] closed-chain hydrocarbons [naphthenes] unsaturated) boiling above 300° C. Their specific gravities lie above 0·840. The influence of the chemical constitution of mineral oils on their lubricating properties has been studied by *A. E. Dunstan and F. B. Thole*,[2] for an account of whose work the original paper must be consulted.

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[1] Lard oil was up to recently the standard oil used by the United States Navy Department when testing lubricating oils.

With the exception of Texas oils, which yield spindle oils of specific gravities from 0·918 to 0·955, the oils of a specific gravity up to 0·900 are almost exclusively products of distillation. The mineral oils derived from crude petroleum are obtained by simple distillation, after the hydrocarbons boiling below 300° C. have been driven off, in a current of steam with or without the aid of vacuum. The mineral oils then pass over practically without undergoing any decomposition. Shale oils and lignite oils are obtained by destructively distilling shale and lignite respectively.

Mineral lubricating oils of a specific gravity exceeding 0·910 are either " concentrated " (" reduced ") oils or distilled oils. The former are obtained by distilling off the lower boiling hydrocarbons from petroleum until a residue of such concentration remains behind that after refining by filtration,[3] etc., it becomes suitable for lubricating purposes. The latter oils are prepared by distilling the residues,[4] obtained after removing the lower boiling hydrocarbons, in a current of steam at the ordinary pressure or in a vacuum, so as to prevent " cracking." Distilled oils containing products of destructive distillation are unsuitable for lubricating purposes.

A patent for the conversion of heavy mineral oils into hydrocarbons of a low boiling point has been taken out by *Zerning*.[5]

Tar oils [6] are chiefly employed as admixtures to " greases " (cp. below).

A description of the details of the manufacture of these oils falls outside the scope of this treatise.

3. BLENDED OILS

Mineral oils are miscible with all fatty oils—excepting castor oil—and liquid waxes. Extensive use is made of this property in practice; hence a large number of commercial lubricating oils consist of a mixture of the two kinds of oils (cp. p. 85). *J. H. Hyde*,[7] following on an observation first made by *Wells and Southcombe*,[8] shows by results obtained with a mechanical oil tester that the frictional coefficient is considerably reduced by the presence of small quantities of rape oil fatty acids out of all proportion to the amount when compared with the quantity of rape oil required to produce a similar diminution. The theory underlying this fact is discussed by *Archbutt.*[1] Castor oil can be made miscible to a certain extent with mineral oils by mixing it first with a fatty oil such as tallow oil. Castor oil on account of its high viscosity and low cold test is used in very large quantities for lubricating aeroplane engines. The solubility of castor oil in some lubricating oils is given in the following table due to *Archbutt* : [2]—

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[1] Mabery and Mathews (*Journ. Amer. Chem. Soc.*, 1908, 992) show that the saturated hydrocarbons, C_nH_{2n+2}, have very little lubricating value; on comparing oils having the same boiling points, but belonging to different series, it is found that the viscosities and specific gravities increase with the decrease of hydrogen in the molecule.

[2] *Journ. Inst. Pet. Techn.*, 1918, 191. Cp. also R. M. Deeley, *Phys. Soc.*, 1919.

[3] The use of liquid sulphurous acid for refining petroleum has been protected under the German patent 216,459.

[4] A distilling apparatus for hydrocarbons has been patented by Turner, English patent 25,832, 1912.

[5] Italian patent 339/202/130,588.

[6] For a lubricating oil from water gas tar, cp. T. O. Kent, German patent 194,372.

[7] *Engineering*, 1921, 111, 708-709.

[8] *Journ. Soc. Chem. Ind.*, 1920, 51 T.

Miscibility of Castor Oil with Mineral Oils

Mineral Oil.	Specific Gravity at 15·5° C.	c.c. of Mineral Oil miscible with 10 c.c. of Castor Oil at 59° F.
Scotch shale . .	0·865	3·7
„ „ . .	0·890	2·45
American . .	0·907-0·912	1·7

In order to render castor oil more readily soluble in mineral oils, *Nördlinger* [3] first heats the castor oil to about 300° C. under ordinary pressure. *Boyer, Cavillon, and Barishac* [4] heat a mixture of castor oil and mineral oil with fatty or mineral acids. *Common* [5] heats castor oil to about 500° F. in an open vessel with about 1 per cent of a reducing agent such as formaldehyde. Other patentees heat the oil to 300° C. in an autoclave.[6] *De Hemptinne* [7] treats a mixture containing 50 per cent of a vegetable or animal oil with the silent electric discharge whereby the mixture is rendered more viscous. It should, of course, be remembered that castor oil thereby undergoes a very important chemical change (cp. Vol. II. p. 406, and below). *W. H. Huxley* [8] passes an electric current through the oil between zinc electrodes in the presence of dilute sulphuric acid. *Common and Hull Oil Manufacturing Co.*[5] propose to render castor oil more miscible with mineral oils by heating castor oil with 4 per cent of formaldehyde to 500° F. in an open vessel (for four hours) until a sample will mix with mineral oils without subsequent separation of the mixture. Oil so treated is then ready to be thickened by blowing at about 250° F. in the usual manner. "Blown oils" (see below) also are largely mixed with mineral oils or with blends of mineral oils and fatty oils. In this connection it may be pointed out that paraffin oils of different origin show striking differences as regards miscibility with fatty oils.

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[1] *Journ. Soc. Chem. Ind.*, 1921, 287 T. Cp. also P. Woog, *Comptes rend.*, 1921, 173, 303 and 387.

[2] Archbutt and Deeley, *Lubrication and Lubricants*, p. 110.

[3] German patent 104,499.

[4] English patent 15,497, 1909; French patent 391,992.

[5] English patent 15,466, 1908; French patent 397,739.

[6] Olwerke, Stern-Sonneborn.

[7] English patent 15,748, 1909; French patent 440,843.

[8] English patent 128,007, 1918.

4. GREASES—SOLID LUBRICANTS

This class of lubricants is prepared from a great variety of fatty oils, solid fats, mineral oils, tar oils, rosin oils, alkali soaps of fatty acids or (and) rosin acids, and from lime- and aluminium soaps of fatty acids or (and) rosin acids. It is a matter of historical interest that *Raecz* was the first to propose the use of the lubricating grease obtained by dissolving lime soap in mineral oil about fifty years ago. These greases are either solid or semi-solid (jelly-like, gelatinous) at the ordinary temperature. In some cases water is introduced together with the soaps ; in other cases weighting substances, or talcum, or plumbago, are mixed into the fatty substance. The examination of these lubricants will be detailed below. To this class of lubricants belong the greases used on the slipways to facilitate the launching of ships (launching tallows). For a mechanical method for their examination cp. *J. J. King-Salter*.[1]

Examination and Valuation of Lubricating Oils

The examination of the **lubricating oils** described under (1), (2), and (3) embraces the application of *physical* and *chemical* methods. These may be supplemented, in the case of large users, by *mechanical* tests.

I. Physical Tests

The physical tests comprise the determination of the specific gravity, the viscosity, the freezing point, the flash point, and of the ignition point.

Specific Gravity.—This is determined as described, Vol. I. Chap. V. It may again be pointed out that this characteristic affords little or no information as regards the lubricating power of an oil. The specific gravity number is, however, useful in determining the kind of work for which a lubricating oil is suitable, and serves as a test of identity (*e.g.* of Borneo oil, which is characterised by very high specific gravity, see Vol. I. Chap. IX.), and assists in directing attention to adulteration with rosin oils or tar oils (cp. Vol. I. Chap. IX.).

Viscosity.—For its determination compare Vol. I. Chap. V. The viscosity number does not furnish an absolute means of determining the lubricating value of an oil, although it enables one to draw certain conclusions.[2] Thus, if the viscosity is low, the film of oil which keeps the bearings of rapidly moving machinery apart is not sufficiently coherent to keep the metal surfaces asunder, and therefore the friction between them is not sufficiently diminished. Again, if the viscosity of an oil be high, the resistance of the film is so great that heating occurs, and the bearings become warm, or even hot, the heat so generated being proportional to the internal friction of the oil, or, in other words, to its viscosity. That oil will prove the best which under given conditions of speed, pressure, and temperature has the lowest permissible viscosity. *Petroff*,[1] rejecting the usual method of determining the viscosity, prefers to measure the internal friction of oils, *i.e.* the absolute viscosity. More recently *Archbutt and Deeley*[2] determined the absolute viscosities[3] of glycerin and water. Since, however, the viscosity, expressed in terms of absolute viscosity, is not likely to replace in the immediate future the customary manner of expressing viscosity; furthermore, since it would follow from *Petroff's* observations that at a given temperature the order of the oils with respect to their internal frictions is the same as that of their lubricating powers and their viscosities as ascertained in the usual manner, the reader must be referred for further information on absolute viscosity to *Archbutt and Deeley's* work, also *Higgins*.[4]

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[1] *Engineering*, 1921, 111, 405.

[2] Pyhälä, *Petroleum*, 1911, 207.

If it is desired to examine the unsaponifiable portion of a blended oil viscosimetrically, the viscosimeters described in Chapter VI. will, as a rule, be found too large. In such cases *Künkler's* viscosimeter, requiring only 30 c.c., may be found useful.

Künkler's[5] viscosimeter (Fig. 1) consists of a sheet brass oil-bath or water-bath, *w*, provided with a copper bottom. The contents of the bath may be heated by a gas burner. The temperature of the heating liquid is read off a thermometer held by *x*. The bath contains the removable stand *d* placed firmly on four legs, and supported by two brackets *h*. In this stand fits the viscosimeter, made of strong glass and consisting of the charging-funnel *k*, the bulb *e* bearing the mark *f*, the capillary tube *c*, the lower bulb *a*, and the ascending tube *b*. The whole apparatus is held in position by the spring-clamp *i*. The temperature of the contents of the viscosimeter is controlled by a thermometer fixed in *k*. The ascending tube *b* is supported by *l*; it is fitted with a tap, *m*, and connected by means of india-rubber tubing with the suction apparatus *r*, in which the mercury used for aspirating the oil is allowed to rise up to the mark *p*. Bulb *t* serves as a receptacle for the mercury. The can *y* is used for warming the oil to the desired temperature.

The apparatus is gauged with a dilute glycerin solution of specific gravity 1·110 at 20° C.; the time required for its outflow at 20° C. is taken as unity. For temperatures up to 100° C. mercury is used as the aspirating liquid; for higher temperatures water is preferred. The heating vessel *w* is filled with water for temperatures up to 100° C.; for temperatures above 100° C. a mineral oil of suitable boiling point is taken.

The test is carried out in the following manner:—Fill *r* up to the mark *p* with the aspirating liquid and heat the bath. In the meantime warm the oil to be tested in the can *y* a few degrees above the required temperature. Take the viscosimeter for a short time, about half a minute, out of the bath so that the air in *a* is somewhat cooled, and then put it back, filling at the same time vessel *e* with the oil up to mark *f*. The air in *a* will then expand so that no oil can enter. Allow the oil in *e* to assume the temperature of the bath, connect the viscosimeter with the aspirator, and open tap *o*. Then open tap *m* and observe accurately the time required by the oil to rise in the ascending tube *b* up to the mark *g*.

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[1] Grossmann, *Die Schmiermittel*, pp. 42-49.

[2] *Lubrication and Lubricants*, p. 126.

[3] Cp. also Chenevier, *Moniteur scient.*, 1898, 785.

[4] *Journ. Soc. Chem. Ind.*, 1913, 568.

[5] *Dingl. Polyt. Journ.* 290, 281.

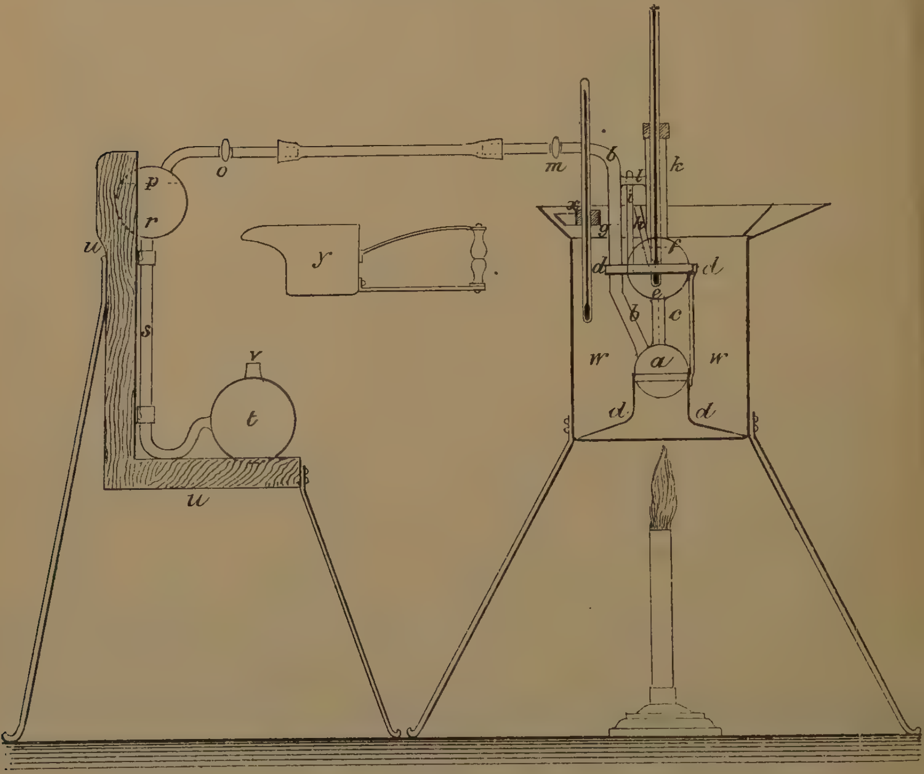

Fig. 1.

For the accurate dimensions of the various parts of the apparatus (made by *C. Desaga* of Heidelberg), the original paper must be consulted.

The following table contains a few viscosimetric numbers determined with this apparatus, placed side by side with the numbers obtained with *Engler's* viscosimeter :—

[TABLE

Kind of Oil.	Künkler's Viscosimeter.						Engler's Viscosimeter.					
	Seconds at			Glycerin Solution, Spec. Grav. 1·110 at 20° C. (66 seconds) =1.			Seconds at			Water at 20° C. (54 seconds) =1.		
	°C.			°C.			°C.			°C.		
	20	50	150	20	50	150	20	50	150	20	50	150
Rape oil, refined	1220	380	...	18·48	5·76	...	660	224	...	12·22	4·15	...
Cod liver oil	760	262	...	11·51	3·97	...	430	165	...	7·96	3·06	...
American lubricating oil, pale, 0·905	905	215	...	13·71	3·26	...	475	140	...	8·80	2·59	...
Russian lubricating oil, pale, 0·908	4320	595	...	65·5	9·01	...	2340	355	...	43·33	6·57	...
American cylinder oil, pale	...	...	750	...	...	11·36	...	...	75	...	...	1·39
” ” ” dark	...	...	1005	...	...	15·23	...	...	95	...	...	1·76
“Valvoline” cylinder oil	...	...	885	...	...	13·41	...	...	85	...	...	1·57

A comparison of the calculated and determined viscosity numbers (*Engler*) and flashing and burning points in oil mixtures is given by *H. Sherman, Gray and Hammerschlag.*[1]

The viscosity of mixtures is always lower than that indicated by calculation. In the case of specific gravity the calculated specific gravity agrees with that found direct.[2]

The viscosity of lubricating oils diminishes rapidly with the increase of temperature; the decrease is, however, much greater in the case of mineral oils than in that of vegetable and animal oils. This is one of the reasons why blends of vegetable and animal oils with mineral oils give better results in practice than do mineral oils alone.

In many cases it is desirable to determine the viscosity of a lubricating oil at high temperatures; if possible, at the temperature which the oil will reach in actual use.

A somewhat high viscosity of a given sample (as compared with the viscosity of a corresponding oil recorded in the tables, Vol. I. Chap. V.) may direct attention to an imperfectly purified oil, containing asphalt-like bodies (p. 92), or to oils thickened with aluminium oleate or with caoutchouc[3] (" oil thickener ").

Freezing Point or Cold-Test.—This is determined by the methods described in Vol. I. Chap. V.

It is necessary to fix by agreement (in contracts) the length of time and the manner in which a sample should be cooled before the cold-test is carried out, since the experimental results depend to a considerable extent on the preliminary treatment of the oil. This holds good of fatty oils as well as of mineral oils. Thus *Holde*[4] has shown that the solidifying points of oils, which were stated by various observers as being below 0° C., will solidify at 0° if allowed to stand at this temperature for several hours. It is well known that stirring assists solidification; hence different results will be obtained according as to whether the oil has or has not been stirred whilst the cold-test was being carried out (cp. Vol. II. Chap. XIV. " Cotton Seed Oil ").

Similar divergencies are noticeable in the examination of mineral oils containing paraffin wax, the separation of paraffin wax taking place at different temperatures according to the manner of manipulation and according to the degree of cooling the oil has undergone previous to its examination. A number of cold-test determinations have been given in Vol. I. Chap. V.

The " cold-test " or setting point of mineral lubricating oils has not so great an importance in this country as in the United States and on the Continent, where the danger exists of machinery being damaged by oil becoming solid in the lubricators. In these countries Railway Companies specify the temperature at which the lubricating oil must remain fluid, and also the manner in which this must be ascertained.

The Scottish Mineral Oil Association directs that the setting point of mineral oils be determined in the following manner:[1]—Place the sample in a test-tube, having a diameter of one inch and a quarter, to the depth of about two inches. Immerse the test-tube in a freezing mixture, and stir the oil slowly with a thermometer, until it has cooled down considerably below the temperature at which solid paraffin wax first appears. Then remove the test-tube from the freezing mixture, stir constantly with the thermometer, and observe the temperature at which the last trace of solid paraffin wax disappears. Repeat the test until concordant results are obtained. The temperature so found is the setting point.

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[1] *Journ. Ind. and Eng. Chem.*, 1909 (i.), 13.

[2] *Chem. Zeit. Rep.*, 1909, 74; cp. also Molin, *Chem. Zeit.*, 1914, 857.

[3] Holde, *Die Untersuchung der Schmiermittel*, p. 122.

[4] *Mitth. a. d. Königl. Tech. Versuchs-Anst.*, 1895, 287.

According to the directions of the New York Produce Exchange, the sample is poured into a beaker, 4 in. deep by 3 in. in diameter, until it is nearly filled. The beaker is immersed in a freezing mixture of specified temperature, the temperature being controlled by a fixed thermometer; a second thermometer is then immersed in the oil, so as to reach half-way down the beaker. The lubricating oil should still flow, on inclining the beaker, when both thermometers register the same temperature. It should be noted that the oil is not stirred and that therefore the conditions obtaining in practice are simulated to some extent, although the time-factor is neglected.

More complicated than the American test is the cold-test prescribed by the Prussian State Railway Direction. According to their rules "winter oil" must remain fluid at −15° C., "summer oil" at −5° C. This is considered to be the case if the oil cooled to −15° C., or −5° C., as the case may be, and subjected to the constant pressure of a water column of 50 mm., will rise in a glass tube of 6 mm. internal diameter at the minimum rate of 10 mm. per minute. The apparatus prescribed for this test is shown in Fig. 2.

The sample, freed from water and mechanical impurities, is introduced into a U-tube of 6 mm. internal diameter (two tubes are shown in the figure). This is immersed in a vessel *h*, filled with the freezing mixture of the specified temperature, and surrounded by vessel *i*, which is also filled with the freezing mixture. The temperature is controlled by a thermometer. The U-tube should stand at least one hour in the freezing mixture without being disturbed, the level of the oil being about 10 mm. below that of the freezing mixture. The tube is then carefully drawn out so far that the level can be observed, when the rubber tube *d* is slipped over its end whilst pinch-cock *e* is open. Close *e* and, by opening pinch-cock *f*, allow a pressure of 50 mm. (generated by pouring water into vessel *a*, in which the weighted funnel *b* is placed and controlled exactly by manometer *c*) to act on the oil.

Flash Point.—The flash point may be determined either by the "open test" or the "close test."

"*Open Test.*"—About 50 c.c. of the oil under examination are placed in a porcelain crucible or in a small wide-necked flask, so as to fill about three-quarters of the vessel. The vessel is embedded in a sand-bath to slightly above the level of the liquid, and a thermometer inserted in the oil. The sand-bath is then heated gradually, so that the temperature may rise slowly, and from time to time a small flame is brought on to the surface of the oil. The lowest temperature at which a slight explosion or " flash " takes place is noted as the flash point. It is advisable to ascertain in a preliminary test the temperature at which the " flash " will take place, and then finally to determine the flash point more accurately. The results obtainable by this method—which is sufficiently accurate for practical purposes, when it is only required to ascertain whether an oil is dangerous or not—vary between 2° and 5° C. In *Scott's* oil tester an electric spark is used for igniting the explosive mixture of vapours. The flash point of a mixture as obtained by direct determination is always lower than that calculated from the flash points of its components.[1]

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[1] *Journ. Soc. Chem. Ind.*, 1891, 347.

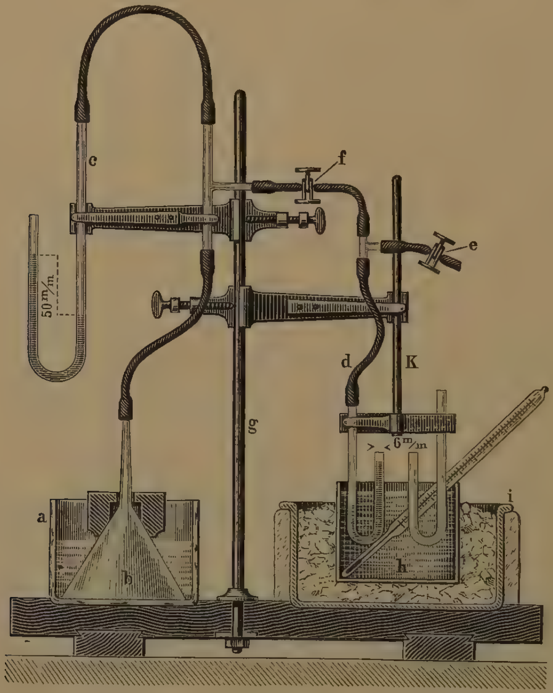

Fig. 2.

It is necessary that the oils be freed from water previous to being tested.

The lowest flash point by the " open test " should be about 175° C. (350° F.) for lubricating oils intended for journals and bearings, and about 260° C. (500° F.) for cylinder oils. The following table, due to *Künkler*,[2] contains a number of flash points of American and Russian lubricating oils :—

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[1] Sherman, Gray and Hammerschlag, *Journ. Ind. and Eng. Chem.*, 1909, 13.

[2] *Journ. Soc. Chem. Ind.*, 1890, 197.

Oils.	Specific Gravity at 17·5° C.	Flash Point °C.	Viscosity (Engler).	
			At 50° C.	At 100° C.
Russian cylinder oils	0·911-0·923	183-238	10·2-16·2	2·0-2·8
" machine oils	0·893-0·920	138-197	5·8-6·3	1·5-1·8
" spindle oils	0·893-0·895	163-167	3·1-3·4	1·4-1·5
American cylinder oils	0·886-0·899	280-283	...	4·1-4·8
" machine oils	0·884-0·920	187-260	4·2	1·6
" spindle oils	0·908-0·911	187-200	3·1-3·3	1·4-1·6

The following table, due to *Lewkowitsch*, gives the flash points and viscosities of some commercial lubricating oils intended for use in motor-car lubrication :—

Specific Gravity at 60° F.	Viscosity Number of Seconds at		Flash Point °F. (Gray).
	70° F.	140° F.	
0·8980	2290	195	366
0·9121	3015	230	404
0·8821	686	100	380
0·9025	2190	217	392
0·9218	2595	342	384

In Germany some railway companies direct that the *Treumann* cup be used for this test.[1] The apparatus is illustrated in Fig. 3.

The proposal by *Marcusson* [2] to fit to the *Treumann* cup a mechanical arrangement for introducing the flame in a manner similar to that adopted in the " close test " apparatus has been adopted by the German Railway Companies.

"*Close Test.*"—When greater accuracy is required than is furnished by the " open test," or in case of a dispute, the adoption of " close test " apparatus is advisable. The *Scottish Mineral Oil Association* [3] prescribes the employment of the *Pensky-Martens* apparatus, which is the one used officially in Germany.[4]

The *Pensky-Martens* apparatus (Fig. 4 and Fig. 5) is modelled on the Abel Petroleum Tester.

E (Fig. 4) is the oil container, which is placed in a metal heating vessel H, provided with a mantle L in order to protect H from loss of heat by radiation. The oil cup E is closed by a tightly-fitting lid (shown in plan 2). Through the centre of the lid passes a shaft carrying the stirring arrangement, which is worked by means of the handle J.[5] In another opening of the cover is fixed a thermometer. The lid is perforated with several orifices, which are left open or covered, as the case may be, by a sliding cover. This can be rotated by turning the vertical spindle by means of the milled head G. By turning G, an opening of the slide can be made to coincide with an orifice in the cover, and simultaneously a very small flame, burning at the movable jet E (Fig. 5), is tilted on to the surface of the oil. This contrivance is shown on a larger scale in plan 2, Fig. 4.

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[1] Cp. Treumann, *Zeits. f. öffentl. Chem.*, 1898, 855.

[2] *Chem. Revue*, 1909, 14.

[3] *Journ. Soc. Chem. Ind.*, 1891, 347.

[4] Cp. also F. A. Courtois' Flash Tester, United States patent 788,250.

[5] A mechanical contrivance for stirring has been described by L. Schmitz, *Chem. Zeit.*, 1909, 58.

The test is performed by filling the oil into the oil cup up to a certain mark, fixing the cover, and heating the oil somewhat rapidly at first, until its temperature is about 30° C. below the expected flash point. The temperature is then allowed to rise very slowly only, by making suitable use of the wire gauze shown in the figures, so that the rise of temperature within half a minute does not exceed about 2° C. From time to time the milled head G is turned and the flame tilted into the oil cup. The temperature at which a slight explosion is produced is noted as the flash point of the oil.

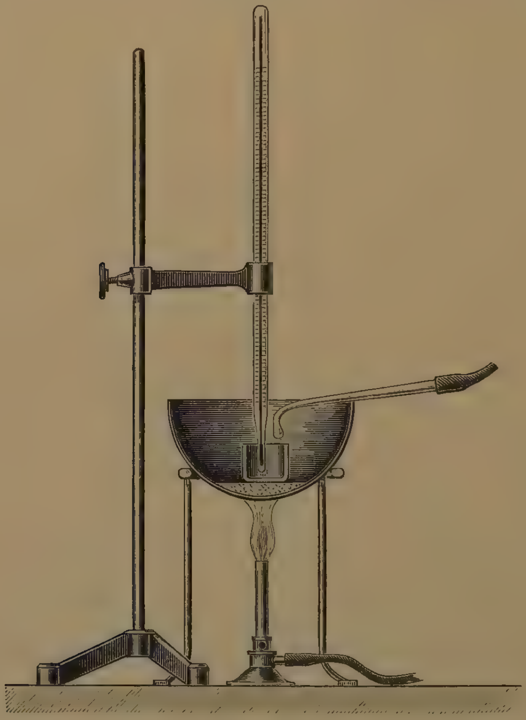

Fig. 3.

In this country *Gray's* apparatus (Fig. 6) is used frequently. It consists of a brass oil cup, A, of 2 in. diameter by 2·2 in. in depth (same dimensions as in the Abel Petroleum Tester). The height to which the cup is filled is indicated by a line cut round the inside; it runs 1½ in. from the bottom. The cup is closed by a tightly-fitting lid, through the centre of which a steel shaft passes to the bottom, carrying two sets of stirrers, one above and the other below the surface of the oil. On the top of the steel shaft there is fixed a small bevelled wheel, H, with milled edge, and geared with a vertical bevelled wheel, G, actuated by a small handle, B. Thus the stirrers are set in motion. The lid is provided with four openings, one of which serves for the insertion of a thermometer, whereas the other three provide means for producing the "flash." These three orifices are, as a rule, closed by a loose flat cover, S, provided with openings which coincide with the ports in the fixed lid when the cover is turned one quarter round. One of the latter is immediately in front of the test-lamp, D, which can be tilted whenever required, whereas the other two ports, one on each side, admit air to produce the explosive mixture.

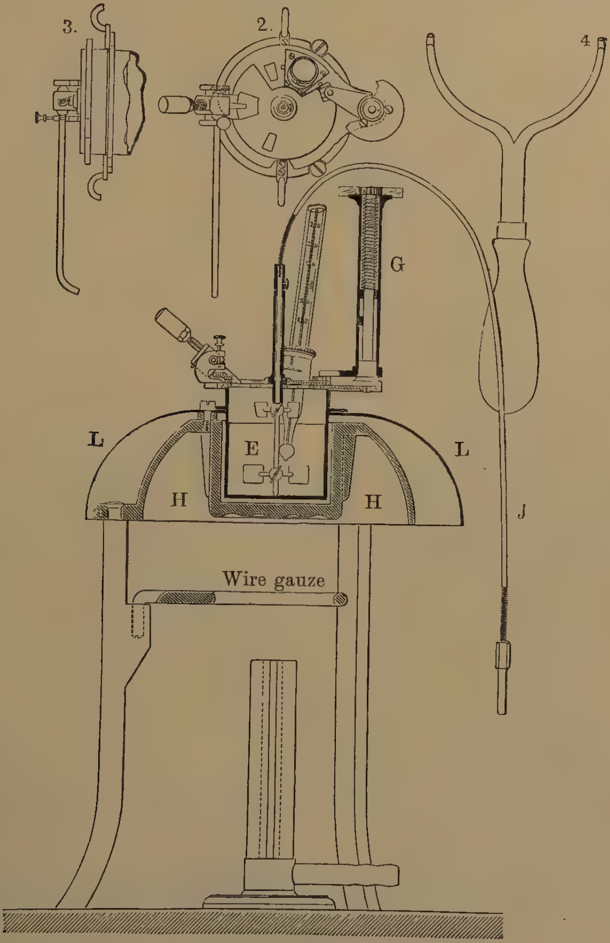

Fig. 4.

To perform the test, fill the cup to the mark with the sample, light the test-lamp and adjust the flame, so that it is about ⅛ in. high; then heat the oil cup by means of a Bunsen burner or a sand-bath, whilst rotating the stirrers, so that the temperature of the oil rises about 5° C. per minute at first, then less rapidly when the point is being approached at which the oil is expected to flash. Whilst the bevelled wheels are in gear the sliding cover is held in its normal position by the spring P. Next draw the horizontal shaft, which has a little lateral play in its bearings, slightly to the right, whereby the stirrers are thrown out of gear. Turn the handle a quarter of a round, when the loose cover is rotated, the ports are opened, and at the same time the test-lamp is tilted into the opening; reverse the handle immediately, whereby the ports are closed automatically. The temperature at which a slight explosion is produced is noted as the flash point of the oil. If no flash was produced, continue the heating, throw the stirrers into gear, and proceed as before.[1]

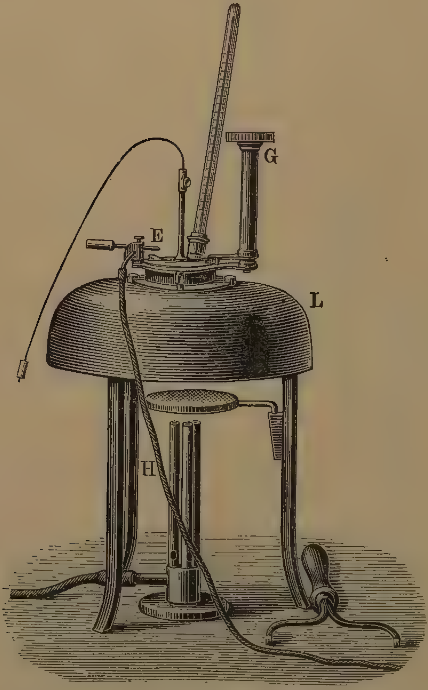

Fig. 5.

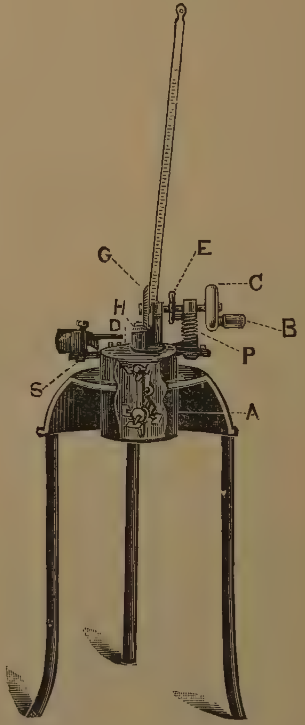

Fig. 6.

Ignition Point, "*Fire Test.*"—The ignition point is the lowest temperature at which the oil will continue to burn after a flame has been brought into contact with its surface for a few seconds. The determination of the ignition point is carried out in a similar manner to that described under "flash point."

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[1] With regard to *Lees*' oil-testing apparatus, see English patent 27,036, 1906 (W. Lees, T. W. Lees, and A. Lees).

A crucible about 40 mm. in diameter and 40 mm. high is filled to within 5 mm. of its brim, and embedded to half its height in a sand-bath. The crucible is heated at first rapidly until the flash point has been reached, then the gas-burner is turned low and the temperature allowed to gradually rise 10°-15° C. above the flash point; after every rise of 2° C. a small flame is approached to the surface until the oil burns quietly. The crucible must be protected from draught by a convenient arrangement.

It should be noted that the "flash point" and "ignition point" furnish no indications whatever as regards the lubricating value of an oil. Their significance lies in that they indicate whether a lubricating oil is suitable under given conditions. Since it so happens that oils having high flash points and ignition points are also the most viscous ones, unwarranted conclusions have been drawn from high flash and ignition points of a given lubricating oil. The presence of free fatty acids causes a considerable depression in the flash point and the ignition point of a lubricating oil. This is brought out by the determinations of *A. Lowenstein and J. Vollertsen.*[1]

Oils intended for use in transformers should be free from moisture[2] and sulphur compounds. For the determination of the electrical resistance of such oils, the papers given in the footnote should be consulted.[3] It should be noted that the electrical conductivity is largely increased by the presence of lime soaps of naphthenic acids.[4]

The London County Council specify the following tests to which an oil intended for filling up the tanks of power switches and transformers must conform:—

Specific gravity at 60° F.	0·859-0·9
Flash point (open)	400° F.
Ignition point	450° F.
Loss at 212° F.	Nil

It also prescribes that the amounts of moisture and acid shall not exceed 0·0009 and 0·01 per cent respectively.

Brauer[5] states that the viscosity and Cold Test should be as low as possible. In order to test the liability of oils intended for use in transformers to become oxidised and form a sludge, *A. C. Michie*[6] places 100 c.c. in a flask of 200 c.c. capacity, having a neck 11½ in. long, which is surrounded by a cold-water jacket; the flask is kept in an oil bath at 150° C. A current of dry air is drawn through the flask for about forty-five hours at the rate of 0·07 cubic feet per hour. The insoluble matter is filtered off, washed with petroleum ether, dried and weighed. In various samples quantities ranging from 0 to 2·5 per cent were found.

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[1] *Journ. Ind. and Eng. Chem.*, 1915, 850.

[2] For a method of determining moisture in transformer oils cp. E. Renegade and J. Clostie, *Comptes rend.*, 1921, 173, 311, also C. J. Rodman, *Journ. Ind. and Eng. Chem.*, 1921, 1149.

[3] Berninger, *Mitt. k. k. Tech. Gewerbe-Museums in Wien*, 1911, 21; Breth, *Petroleum*, 1911, 290; Tobey, *The Electrician*, 1911, 491; Digby and Mellis, *Times Eng. Supplmt.*, 1910, March 30.

[4] D. Holde, *Journ. Chem. Soc.*, 1915, 108, 136.

[5] *Chem. Revue*, 1914, 136.

[6] *Journ. Inst. Elect. Engineers*, 1913, 51, 213. Cp. also P. Digby, *ibid.* 1915, 53, 146, and C. E. Waters, *Journ. Ind. and Eng. Chem.*, 1921, 901.

L. Radcliffe and C. Polychronis[1] have attempted to establish a relationship between the iodine absorption and the liability of an oil to form sludge with encouraging results.

II. Chemical Tests

The general *chemical tests* have for their object the identification of the oil; the examination for purity (absence of adulterants); the detection and determination of water; the determination of ash; the determination of free acid; the liability to "gum" or to become oxidised; the liability to spontaneous combustion; the determination of loss by evaporation; the determination of paraffin wax; the detection of "deblooming" agents, and in some cases of colouring matter.

In the determination of the loss by evaporation in order to get comparable results it is essential that the same weight of oil be used for each test and also that the determination is carried out in a vessel having the same dimensions. *Waters*[2] recommends a brass vessel 5 cm. internal diameter and 3 cm. in height, 5 grms. of oil being used for each test.

Before a lubricating oil is tested it must be freed from grit or solid tarry particles, by filtering through filter paper or a sieve of very fine mesh. In some cases it may be of assistance to dissolve the lubricating oil in petroleum spirit or in benzene.

The methods employed for the **identification** of fatty oils and liquid waxes have been described in previous chapters. The ascertaining of the origin of a mineral oil from petroleum is but rarely required. Expeditious methods for the discrimination between hydrocarbons derived from American, Russian, Galician, Roumanian, etc., petroleums have not yet been worked out, as the chemical composition of the hydrocarbons in the *high boiling* portions is practically unknown as yet.[3] According to *Chercheffsky*[4] the determination of the critical temperature of solution in alcohol and the turbidity temperature with acetic anhydride will throw some light on this problem, the highest values being obtained for Pennsylvanian oils, and the lowest for Roumanian.[5] Shale oil hydrocarbons seem to be characterised by the somewhat high amounts of bromine they absorb, as compared with mineral oils derived from petroleum: this is due to the presence of a considerable amount of olefinic hydrocarbons. In the absence of methods allowing a discrimination between shale oil and lignite oils,[6] physical indications, such as colour, fluorescence, smell, and also taste, afford safer guidance in ascertaining the origin of these oils than has been furnished hitherto by purely chemical methods. The identification of *tar oils* is easy (cp. Vol. I. Chap. IX.). Tar oils are used alone for lubricating suction gas engines (in coke works, gas works, and suction gas installations generally), their function, besides acting as lubricants, being to retain in solution the tarry vapours which are carried forward with the gases.

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[1] *Journ. Chem. Soc. Ind.*, 1916, 340. Cp. also C. J. Rodman, *Trans. Amer. Electrochem. Soc.*, 1921, 105.

[2] *Journ. Ind. and Eng. Chem.*, 1913, 394.

[3] Cp. Aisinmann, *Chem. Revue*, 1897, 162.

[4] *Compt. d. r. Acad. d. Sciences*, 1910, 1338.

[5] Cp. *Mitt. a. d. Königl. Materialprüfungsamt*, 1909, 27.

[6] Cp. *Jahrbuch d. Chem.*, 1897 (viii.), 384, 388.

Blended oils, i.e. oils consisting of a mixture of fatty oils (" blown oils," see below), liquid waxes, and mineral oils, are identified by the general methods of analysis given in Vol. I. Chapters VI.-IX. Such oils are largely used, especially for the lubrication of steam cylinders, since it has been ascertained by extensive practical experience that blended oils are more economical, less oil being consumed than when mineral oils alone are employed. This is due to the fact that mineral oils are more readily volatilised than fatty oils.

Small quantities of fatty oils in mineral oils are detected by ascertaining whether the sample has a definite saponification value. The absolute quantity of the fatty oil can be readily ascertained by isolating the fatty acids, determining their mean molecular weight, and calculating therefrom to glycerides. If the amount of fatty oils be very small, the proportion of glycerol may be determined in a somewhat large quantity of the sample. If liquid waxes be present, the fatty acids must be calculated to esters.

The presence of " blown oils " is detected in the first instance by ascertaining the proportion of " oxidised acids " (see Vol. I. Chap. VIII.), and next by determining the acetyl value of the isolated fatty acids (cp. Chap. VIII. and table given under " Blown Oils "). It should, however, be remembered that a high acetyl value may also be due to the presence of castor oil. (In this connection it may be pointed out that mixtures containing castor oil are not infrequently met with in commerce.[1]) With regard to the value of " blown oils " as lubricants, cp. below. The " blown oils " are frequently met with in lubricating oils for marine engines. Blown oils are also frequently employed as an ingredient in the preparation of lardine (a fancy name, which has also been used for butter adulterants, and must not be confounded with them. Cp. also " Lardeen," p. 30).

Rosin Oils.—The determination and examination of the *unsaponifiable* matter—rosin oils, tar oils, etc.—is of great importance; methods of detecting these oils in the unsaponifiable portion have been described, Vol. I. Chap. IX.

The *Liebermann-Storch* reaction may be supplemented by polarimetric examination. Rosin oils are dextro-rotatory; hence the presence of large quantities of rosin oils will be most readily detected by examining the unsaponifiable matter in the polarimeter. *Valenta* found in the case of a number of samples of rosin oils in *Mitscherlich's* polarimeter, for a length of 100 mm., rotations varying from 30° to 40° (dark specimens were previously clarified by means of charcoal). *Demski and Morawski* likewise found the rotation about 50°. Formerly mineral oils were thought to be without action on the plane of polarised light, a few samples only having been found dextro-rotatory, causing a deviation of 1° 1′ to 1° 6′.[1] More recently the property of rotating the plane of polarised light has been observed in a notable number of specimens of lubricating oils from American, Russian, and Galician sources. The somewhat too hasty deduction made by some observers, viz. that optical activity is a general property of lubricating oils derived from petroleum, is, however, not borne out by facts, for both optically active and inactive oils are obtained from petroleum fields lying practically side by side.[2] Nor has the generalisation, made rather prematurely, viz. that all mineral oils are dextro-rotatory, been borne out by facts, for a Javanese mineral oil examined by *Engler* was found laevo-rotatory. Still, such optical rotations as have been observed are too small to interfere with the decided rotation exhibited by a specimen which contains rosin oil. Since several vegetable oils contain optically active foreign substances, which pass into the unsaponifiable matter, due care must be exercised. It should further be borne in mind that hydrocarbons resulting from the destructive distillation of wool fat also exhibit optical activity (*Lewkowitsch*).

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[1] English patent 2680, 1906, Crowley and Payne.

A new method of detecting small quantities of mineral and rosin oils in fatty oils due to *Outerbridge* [3] depends upon the fact that these oils show a fluorescence "bloom" when examined by reflected light. *Outerbridge* recommends, for this purpose, the light from an enclosed arc. It has, however, been pointed out by *Walker and Boughton* [4] that some samples of linseed oil and other vegetable oils show a marked fluorescence and also that a linseed oil which showed no fluorescence in the raw state, after heating to 300° C. and cooling was strongly fluorescent.

The quantitative determination of rosin oils in the "unsaponifiable portion" is a difficult problem, and cannot be solved satisfactorily in the present state of our knowledge. According to *Storch* [5] 10 to 15 grms. of the unsaponifiable matter (carefully freed from fatty oils) are gently warmed in a flask with five times their weight of 96 per cent alcohol, and allowed to cool. The alcoholic solution, which will contain all the rosin oil present, is then transferred to a tared Erlenmeyer flask, about 7 c.m. high; the undissolved mineral oil is again washed, without agitating, with a few c.c. of 96 per cent alcohol, which are added to the first solution. The Erlenmeyer flask is now placed in a beaker (to prevent too rapid condensation) and heated on a water-bath until the residue in the flask is free from bubbles. After cooling, the residue is weighed. The weight of this residue (A) represents that of the rosin oil *plus* that portion of mineral oil which has been dissolved by the alcohol. To remove the bulk of the dissolved mineral oil, the residue (A) is next treated with ten times its weight of alcohol, and the solution heated on the water-bath in the same manner as before to remove the alcohol, when a second residue (B) is obtained, which still retains a small quantity of mineral oil. The necessary correction for this amount is found in the following manner :—Suppose 11·2 grms. of the sample have been treated with 50 grms. at first, and subsequently the residue A with 15·5 grms. of alcohol. Let the weight of A be 1·51 grms., and that of B 1·15 grms., then 50 – 15·5 = 34·5 grms. of alcohol had dissolved 1·51 – 1·15 = 0·36 grm. ; hence 15·5 grms. had dissolved 0·162 grm. of mineral oil. There are therefore present in the sample 1·15 – 0·162 = 0·988 grm., or 8·8 per cent of rosin oil. The true quantity lies between the weight of B and the corrected number.

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[1] $[\alpha]_D = +1°$. Cp. Soltsien, *Chem. Zentralbl.*, 1898, ii. 455; *Zeits. f. angew. Chem.*, 1904, 893; cp. further Zaloziecki and Klarfield, *Chem. Zeit.*, 1907, 1155; 1170.

[2] Cp. Lewkowitsch, *Chem. Zeit.*, 1908, 54; *Jahrbuch d. Chem.*, 1907 (xvii.), 416.

[3] *Proc. Amer. Soc.*, for testing materials, 1911, vol. xi.

[4] *United States Journ. Eng. Chem.*, 1912.

[5] *Journ. Soc. Chem. Ind.*, 1891, 276.

Walker and Robertshaw[1] examined in the author's laboratory the various methods proposed for the quantitative determination of rosin oils. The process proposed by *McIlhiney*[2] for the estimation of rosin oils in fatty oils is based on the fact that the latter yield very low bromine substitution numbers, whereas rosin oils are characterised by high substitution numbers. *Walker and Robertshaw*, however, ascertained that the reaction taking place when bromine is allowed to act on rosin oils depends so much on variations of time, temperature, and other not yet fully recognised conditions, that it would appear a hopeless task to determine rosin oil quantitatively by this method in a mixture of rosin oil with mineral oil.

The method proposed by *Holde*[3] for discriminating and determining rosin oil when admixed with mineral oils has also been shown in the author's laboratory to lead to uncertain results. Thus genuine rosin oils freed from rosin acids yielded considerable quantities of unsaponifiable portions which might have been easily mistaken for mineral oil.[4]

The best method for determining rosin oil in mineral oil is *Valenta's* process, as has been confirmed by experiments of *Walker and Robertshaw*[5] in the author's laboratory. *Valenta's*[6] process for detecting rosin oils in presence of mineral oils is based on the difference of their solubilities in glacial acetic acid at 50° C., a number of experiments made with various mineral oils having shown that 100 grms. of glacial acetic acid dissolve 2·6 to 6·5 grms. of mineral oil, whilst under the same conditions 16·9 grms. of rosin oil are dissolved. The same relation is expressed by stating that 10 c.c. of glacial acetic acid dissolve 0·2833 to 0·6849 grm. of mineral oil and 1·7788 grms. of rosin oil. To perform *Valenta's* test 2 c.c. of the unsaponifiable matter are mixed in a test-tube with 10 c.c. of glacial acetic acid, and the tube, loosely closed with a cork, is immersed in a water-bath, having the temperature of 50° C., for five minutes, the contents being repeatedly shaken during that time. The mixture is then filtered through a moistened filter, and the middle portion of the filtrate is collected. Part of this is weighed off accurately, and the amount of acetic acid therein determined by titration with normal caustic soda. The difference between the weight of the acid taken and the weight thus found is the amount of oil dissolved. *Allen*[1] points out that rosin acids if present in the rosin oil influence the solubility, and render the alkalimetric determination of the acetic acid inaccurate. He proposes, therefore, to neutralise the greater part of the acetic acid, dilute with water, and extract the rosin oil by agitation with ether.

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[1] *Analyst,* 1902, 238.
[2] *Journ. Amer. Chem. Soc.*, 1899, 1084; cp. also Vol. I. Chap. X.
[3] Cp. Lunge, *Chem. Tech. Untersuchungsmethoden*, 6th edition, vol. iii. p. 633.
[4] Lewkowitsch, *Analyst*, 1903, 183; cp. also Utz, *Chem. Revue*, 1906, 48.
[5] *Analyst*, 1902, 238.
[6] *Journ. Soc. Chem. Ind.*, 1884, 643.

Walker and Robertshaw, in the author's laboratory, found the proportion of rosin oil dissolved by acetic acid from two specimens of genuine rosin oils 16·8 and 16·6 per cent respectively, which agrees well with *Valenta's* figure of 16·9 per cent. A mineral oil which gave in *Valenta's* test 4·4 per cent (as compared with *Valenta's* numbers of 2·6-6·5 per cent) was then mixed with an equal volume of a rosin oil of which 16·8 per cent was soluble. The mixture gave, in *Valenta's* test, 10·84 per cent of dissolved oil, theory requiring 10·59 per cent.

A similar method based on the solubility of rosin oils in acetone—with which they are miscible in all proportions, whereas mineral oils require several volumes of acetone for complete solution (*Demski and Morawski*,[2] *Wiederhold*[3])—has not yet been worked out quantitatively. Nor is it likely to lead to useful results, for Borneo mineral oil of specific gravity 0·97 to 0·99 simulates rosin oil not only in specific gravity, but also in that it is very readily soluble in an equal volume of acetone.[4] It is, however, easy to differentiate Borneo oil from rosin oil by the *Liebermann-Storch* reaction. *Schwarz*[5] used acetone to separate mineral oils from asphalt.

Finkener's[6] proposal to differentiate rosin oil from mineral oil by means of a mixture of 1 volume of chloroform and 10 volumes of alcohol of specific gravity 0·8182 at 15·5° C. has not yet been worked out to a quantitative method. It may suffice, therefore, to mention that *Finkener* found that rosin oils are soluble in 10 volumes (according to *Holde*[7] 12·5 volumes, *Wiederhold*[3] 16 volumes, and *Utz*[8] 17 volumes) of this mixture, whereas mineral oils are insoluble even in 100 volumes of the mixture.

Tar Oils.—During recent years adulteration of lubricating oils with coal tar oils and (especially on the Continent) lignite tar oils has been practised. The most useful method of detecting these oils and determining approximately their proportions is that proposed by *Valenta* (see Vol. I. Chap. IX.), based on the solubility of these oils in dimethylsulphate.

Mixture of Mineral Oils with Tar Oils and Rosin Oils.—*Valenta* states that also from such mixtures the tar oils can be approximately separated and determined by means of dimethylsulphate (Vol. I. Chap. IX.). It is, however, doubtful whether, in view of the strictures that attach to this method, this problem can be solved satisfactorily;

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[1] *Com. Org. Anal.* ii. 465.

[2] *Journ. Soc. Chem. Ind.*, 1886, 179.

[3] *Journ. f. prakt. Chem.*, 1893 (47), 394.

[4] Jenkins, *Analyst*, 1902, 240.

[5] German patent 232,794.

[6] *Zeits. f. analyt. Chem.*, 1887, 652.

[7] *Chem. Revue*, 1898, 51.

[8] *Chem. Revue*, 1906, 48. Carbontetrachloride is useless for this purpose, as both mineral and rosin oils dissolve in this menstruum in every proportion.

hitherto no experiments have been published in this connection. The following *modus operandi* would suggest itself:—Remove the tar oils (as far as is practicable) by treatment with dimethylsulphate, saponify the dimethylsulphate solution with alcoholic soda or potash, and isolate the dissolved tar oil for further examination. The undissolved portion, consisting mainly of petroleum hydrocarbons and rosin oils, would then be treated by the methods described under "Rosin Oils," p. 85. Mineral oils hardly dissolve any dimethylsulphate; it would, however, be advisable to subject the mineral oil and rosin oil mixture to saponification in order to remove any dissolved dimethylsulphate before resorting to further examination.

Detection and Determination of Water.—Oils having a turbid appearance, as a rule, contain water. In the case of mineral oils turbidity may also be caused by separated paraffin wax; this will disappear on warming the sample. Water is readily detected by heating a sample in a test-tube, when frothing or bumping will reveal its presence. In the case of fatty oils the determination of water is carried out as described, Vol. I. Chap. IV. In the presence of mineral oils, especially those of comparatively low boiling points, the determination of water in the usual manner may easily lead to deceptive results, inasmuch as oils of low boiling points are volatilised with the water vapours. Hence, due care must be exercised. The proportion of water is best determined by dissolving a somewhat large quantity of the sample in petroleum ether, so that the water may settle out on standing.

The distillation [1] of the substance with a mixture consisting of one part of toluene with two parts of xylene, will be found useful. The distillate is collected in a measuring cylinder and the volume of water read off direct. The water may also be determined in a centrifugal machine.

Determination of Ash.—The ash is determined by igniting an accurately weighed quantity of the sample in a platinum dish and weighing the residue. In pure lubricating oils the ash should be *nil*. A definite residue may point to the presence of soda, potash, lime, or aluminium soap. In that case the residue will exhibit a strongly alkaline reaction to indicators. The presence of alumina in the ash would indicate that aluminium oleate ("oil thickener") had been added.

Schweitzer and Lungwitz [2] recommend as a reagent for the detection of soaps in lubricating oils a saturated solution of metaphosphoric acid in absolute alcohol. In the presence of soaps a flocculent precipitate is observed.

Determination of Free Acids.—The determination of free acids is of considerable importance in the examination of lubricating oils. The estimation of the free fatty acids is carried out in the manner described in Vol. I. Chap. VIII. *Loebell* recommends the use of a mixture consisting of two parts of benzene and one part of 96 per cent alcohol.[3]

[1] *Chem. Zeit.*, 1913, 353. Cp. also H. Shrewsbury, *Analyst*, 1915, 529.

[2] *Journ. Soc. Chem. Ind.*, 1894, 1178.

[3] *Chem. Zeit.*, 1911, 276.

If the lubricating oil be a fatty oil, acidity may be due either to free fatty acids or to incomplete removal of mineral acids, left in the oil in consequence of faulty washing after refining. Mineral acids are detected by shaking the sample with water to which a drop of methyl-orange solution has been added.

In the same manner mineral oils are tested for traces of inorganic acids. Naphthenic acids, so-called petroleum acids,[1] are not removed by washing with water. Their proportion is determined by shaking 100 grms. of oil with 50 c.c. of decinormal alkali containing about 50 per cent of alcohol, and titrating back the excess (*Zaloziecki*[2]). In case the presence of sulphonated oils, produced by the action of concentrated sulphuric acid whilst refining the oils, be suspected, 50 grms. of the oil should be boiled under a reflux condenser with strong hydrochloric acid. The aqueous layer is then tested for sulphuric acid.[3]

A definite acidity may also be due to added rosin (cp. Vol. II. "Linseed Oil," p. 71).

With regard to the permissible amount of free fatty acids in lubricating oils, opinions differ. As a rule, railway companies specify in their contracts the *maximum* amount of free acid. The larger the proportion of free acids in an oil, the greater is its liability to corrode the metal surfaces of the lubricated journals. The experiments made by *I. Redwood,*[4] *Aisinmann,*[5] *and Donath,*[6] do not permit one to draw the conclusion that lubricating oils would exert the same action on metals in practice as they do in laboratory experiments. Hence these experiments need not be detailed here.

It should be borne in mind that fatty oils undergo hydrolysis in high-pressure steam cylinders, as of course also in steam engines using superheated steam, and that the fatty acids thus set free will corrode the iron, with formation of metallic soaps. This is one of the reasons why fatty oils are no longer used alone for lubricating high-pressure steam cylinders. Metallic soaps formed by the action of the liberated fatty acids on the metal are somewhat soluble in mineral oils (cp. "Metallic Soaps," below), and are therefore less likely to cause obstructions (by forming the well-known deposits found in cylinders) than when fatty oils alone are used.

The opinion held generally that mineral oils do not attack metals is based more on chemical *a priori* deductions than on practical experience. *Worrall and Southcombe*[7] concluded from experiments made on a laboratory scale that mineral oils do not undergo a chemical change in a steam cylinder below 750° F—provided, of course, the steam does not contain a notable quantity of air[8]—and further that the iron deposits in steam cylinders were due to oxide of iron particles carried over mechanically by steam and cemented together by resinified oil. The latter observation is quite correct, for it is well known that many deposits found in steam cylinders contain preponderantly mineral substances which can have only been carried over with the steam (by "priming"), but the fact must not be overlooked that on exposure to air—which is always present in steam—mineral oils do suffer oxidation, the extent of which depends largely on the care used in refining them. This has been shown by *Southcombe*[1] by blowing hydrocarbon oils with air saturated with water in the presence of finely divided metals. Appreciable amounts of asphaltic bodies were formed, as is shown by the following table:—

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[1] Cp. Schulz-Kolin, *Chem. Zeit.*, 1908, 596.

[2] *Chem. Revue*, 1897, 37.

[3] Cp. also Heusler and Dennstedt, *Zeits. f. angew. Chem.*, 1904, 264.

[4] *Journ. Soc. Chem. Ind.*, 1886, 362.

[5] *Dingl. Polyt. Journ.* 294, 65.

[6] *Ibid.* 294, 186.

[7] *Journ. Soc. Chem. Ind.*, 1908, 308; cp. also Künkler and Schwedhelm, *Seifensieder Zeit.*, 1908, No. 14.

[8] Cp. also Schreiber, *Zeits. f. angew. Chem.*, 1910, 103.

Oil.	Time of Blowing.	Temperature.	Soluble in Ether (insoluble in Petrol).	Soluble in Carbon Bisulphide (insoluble in Ether).	Organic Acids.
	Hours.	° C.	Per cent.	Per cent.	Per cent.
A	56	150	0·75	0·11	0·25
B	56	150	1·0	0·2	0·16
A	94	120-130	1·6	0·35	0·4
C	112	90	2·5	0·22	0·38

This does not only hold good of shale oils, but in general of American, Russian, and other mineral oils.[2] Further experimental evidence would therefore seem to be necessary. Prolonged exposure to sunlight also causes the formation of asphaltic bodies, as is shown by *Waters*,[3] who found amounts of matter insoluble in ligroin varying from 0·77 to 2·86 per cent.

Liability to "gum."—A good lubricating oil should neither dry on exposure nor "gum" (causing more fuel to be consumed in consequence of the drag upon the machinery), nor have a tendency to become acid. Satisfactory methods for ascertaining the liability of a lubricating oil to "gum" have not yet been worked out. Since oils belonging to the class of drying oils, as also fish and blubber oils, rosin oils, and to a smaller extent also the semi-drying oils of the cotton seed oil group, readily absorb oxygen, and thereby "thicken" or "gum," the unsuitability of these oils for lubricating purposes is evident. The detection of the presence of such oils in a sample has been described in Vol. II. Chapter XIV. An examination of the sample by the methods described in Vol. I. Chapter VII. under "Oxygen Absorption Test" may in some cases prove of assistance.

Gill[4] proposes to determine the gumming properties of lubricating oils with nitro-sulphuric acid (prepared by saturating sulphuric acid of 76° Bé, containing a few drops of nitric acid, with nitric oxide at 0° C.). The amount of tarry matter formed thereby is stated to stand in a definite relation to the oxygen absorption as ascertained by *Fox's* method. This method, of which details were given in former editions of this work,[1] consists in determining the oxygen absorbed on heating an oil in a sealed tube with oxygen gas.

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[1] *Journ. Soc. Chem. Ind.*, 1911, 261.

[2] Cp. Ostrejko, *Journ. Soc. Chem. Ind.*, 1896, 26, 345, 645; Holde, *Die Untersuchung der Schmiermittel*, 1897, p. 88; Steuart, *Journ. Soc. Chem. Ind.*, 1899, 239.

[3] *Journ. Ind. Eng. Chem.*, 1910, 451.

[4] *Journ. Amer. Chem. Soc.*, 1902, 690.

Badly refined oils have a tendency to resinify easily. Impurities due to faulty refining may be looked for and identified by one of the following methods. It should, however, be noted that in some cases certain impurities are purposely left in the oils, since complete removal of the asphalt-like and mucilaginous substances, occurring naturally in the crude oils, tends to reduce the viscosity and, in the eyes of some users, the apparent lubricating value. *Martens* advises to shake equal measures of the sample and of sulphuric acid, specific gravity 1·53 at the ordinary temperature. A pure oil should yield a colourless or, at most, a slightly yellow acid layer; there should be no separation of black flocks in the oil, nor should it be coloured brown. If the acid remains colourless, or is but slightly coloured, the experiment should be repeated at 100° C.; even under these conditions pure oils should not turn brown. (In the presence of fatty oils this treatment with sulphuric acid would lead to altogether unreliable results.) Attempts have been made to convert this test into a quantitative one, in the examination of mineral oils, by operating as follows:—

20 c.c. of the sample are shaken in a graduated stoppered cylinder with 10 c.c. of concentrated sulphuric acid and 20 c.c. of petroleum ether; the increase in volume of the acid is read off after separation into two layers has taken place. Oils of good quality should yield to the acid no more than 1·2 to 2·4 c.c., *i.e.* 6 to 12 per cent.[2] But it must be understood that these results lead to rough approximations only, as the "naphthenes," the characteristic hydrocarbons of the Russian petroleum, are soluble in concentrated sulphuric acid. *Holde*[3] showed that by treating lubricating oils with a mixture of alcohol and ether (3 : 4) resinous or "soft asphaltic" bodies containing oxygen are precipitated, whereas by petroleum ether (300-500 c.c. for 2-5 grms. of oil) "hard asphaltic" substances are precipitated. Hitherto no reliable quantitative method has been worked out.[4] It should be pointed out that petroleum ether is incapable of precipitating the total amount of "asphaltic" bodies.

A discussion on the difference between natural asphaltum and the asphaltic bodies left after the distillation of petroleum falls outside the scope of this work, and the reader must, therefore, be referred to the papers mentioned in the footnote.[5]

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[1] Cp. *Chemical Analysis of Oils, Fats, and Waxes*, 2nd ed. p. 714.

[2] Cp. also Kissling, *Chem. Zeit.*, 1905, 1086, K. Charitschkoff, *Petroleum*, 1914, 9, 690, and L. Gurwitsch, *ibid.* 1914, 9, 1303.

[3] *Mitth. Königl. Techn. Vers. Anst.*, 1895, 174; 1902, 253; 1903, 57; M. Gary, *Mitt. K. Materialprüf.*, 1916, 210.

[4] Holde, *Die Untersuchung der Schmiermittel*, p. 183; 2nd edition, p. 19. Cp. also Aisinmann, *ibid.*, 1895, 282; Singer, *Chem. Revue*, 1897, 93; Holde and Eickmann, *Petroleum*, 1907, 1077; Holde, *Mitt. a. d. Königl. Materialprüfungsamt*, 1909.

[5] Pailler, *Journ. Ind. Eng. Chem.*, 1914; Marcusson, *Chem. Zeit.*, 1914, 813, 822; Rosenthal, *Zeits. f. angew. Chem.*, 1914, 242; C. Richardson, *Journ. Ind. and Eng. Chem.*, 1915, 463, *ibid.* 1916, 4, 319 and 493; R. Bratter, *Zeits. f. angew. Chem.*, 1916, 47; E. Graefe, *ibid.* 1916, 21; H. Loebell, *Chem. Zeit.*, 1914, 18; J. Marcusson, *Mitt. K. Materialprüf.*, 1914, 419, 1916, 40, and *Zeits. f. angew. Chem.*, 1916, 349.

In the presence of paraffin wax the latter would be precipitated together with the " asphaltic " substances. *Lecocq*[1] recommends therefore to remove the paraffin first by distillation in a current of steam.

Formerly the question of determining quantitatively those impurities which are likely to lead to " gumming " did not have the same importance it has at present, for in the older methods of lubrication fresh oil continually displaced oil that had passed between the lubricated journals, and thus products of oxidation were washed away. But since " rings " or " chain lubrication " has come into vogue, and the number of cases increase daily where the oil remains a long time in contact with the material it is intended to protect (as in turbines, transformers, etc.), the accumulation of oxidised substances producing a sediment in the oil has given added, and in some cases even prominent, importance to chemical methods of detecting and determining these impurities. As satisfactory methods for analytically expressing the " gumming " property have not yet been worked out, it must suffice here to point out some further attempts that have been made recently in this direction.

Kissling[2] suggests heating 50 grms. of oil in an oven to 125°-135° C. for five days of twelve hours each, and then to transfer (with the aid of petroleum ether) the oil, together with any sediment that may have formed, to a 500-c.c. flask. After the flask has been made up to the mark with petroleum ether, and has been allowed to stand for twelve hours, the insoluble matter is filtered off, washed with petroleum ether, dried, and weighed. The amount of insoluble matter, judged to be " asphalt pitch," was found to range in twenty-one representative lubricating oils from 0·044 to 3·114 per cent. (*Kissling* proposes to term this percentage number, " resinification number."[3])

Another quantitative method proposed by *Kissling*[4] directs to determine in 50 grms. of lubricating oil the amount of substance that can be extracted by shaking with 50 c.c. of an alcoholic soda solution (made up by mixing 50 grms. of aqueous soda solution, containing 7·5 per cent $NaOH$, with 50 grms. of 99 per cent alcohol) at 80° C. in a bottle provided with a long cooling tube. The aqueous solution is then withdrawn, shaken out with petroleum ether to remove any emulsified or dissolved oil,[5] and then treated with hydrochloric acid, and shaken out with benzene. The benzene solution is evaporated to dryness, and the residue weighed. (The percentage so obtained is termed by *Kissling* " tar number.") The quantity of tarry substances, in a number of commercial lubricating oils, amounted to from 0·023 to 1·451 per cent. *Loewy*[6] determines the tarry matter in vulcan oils by shaking 10 c.c. of the oil with 10 c.c. benzene and 3 c.c. of concentrated sulphuric acid. After standing for one hour the increase over 3 c.c. is read off. According to the Hungarian Railway specifications the amount of tarry matter in these oils must not exceed 25 per cent.

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[1] *Bull. Soc. Chim. Belg.*, 1908 (22), 81.

[2] *Chem. Zeit.*, 1906, 932. Cp. also Schreiber, *Zeits. f. angew. Chem.*, 1905, 727.

[3] Cp. *Chem. Revue*, 1909, 3.

[4] *Chem. Zeit.*, 1907, 328; 1909, 522.

[5] The oil so shaken out contained in all cases a little mineral oil. It had a viscous, almost resinous, consistence, and contained as an average 3·25 per cent of sulphur, whereas the residue obtained on evaporating the benzene solution furnished 1·90 per cent of sulphur only.

[6] *Chem. Zeit. Rep.*, 1910, 6.

These proposed methods require further working out, as they appear to furnish useful data in judging the extent to which lubricating oils have been purified. In this connection it may be mentioned that several patents have been taken out for the removal of the "resin-like" and "asphaltic" substances in mineral lubricating oils by means of volatile solvents,[1] and that the specifications of the German railways stipulate that dark-coloured oils, lubricating oils (used as axle oils, cylinder oils, etc.), must be completely soluble in 40 volumes petroleum ether of specific gravity 0·60 to 0·70. It has been stated above that petrol ether does not precipitate all "asphaltic" substances, and experience has shown that the amount of precipitate varies with the quality of the petroleum ether. Instead of rejecting a method which leads to capricious results the (somewhat clumsy) device has been adopted to define the composition of the petroleum ether to be used as follows :—"The normal benzine" should be as free as possible from unsaturated and from aromatic hydrocarbons, and should have a specific gravity of from 0·695 to 0·705, and should boil between 65-95° C. No more than 5 per cent should boil above 95° C.

Another impurity which is also precipitated by the alcohol-ether mixture is **caoutchouc** (Para rubber), which is added to lubricating oils in order to raise their viscosity. It should, however, be borne in mind that special lubricants, *e.g.* those intended for greasing steam taps, are openly sold as containing caoutchouc (see below).

Since fatty oils, which exhibit a pronounced tendency to "gum," are also those which are liable to spontaneous combustion, the behaviour of a fatty lubricating oil in this respect may be determined by means of the "Cloth Oil Tester" (see Wool Oils, below).

Richardson and Hanson[2] propose to heat a lubricating oil under examination to 400° F. in air or steam, in a specially constructed copper oven. They then determine the viscosity of the oxidised oil and compare it with that of the original. The increase in viscosity is stated to serve as a guide in judging the suitability of an oil as regards gumming property.

A practical "gumming test" prescribed by the United States Naval Department is the following :—

Using a single wick, one half-pint brass oil cup, and maintaining the oil at about 140° F., practically equal quantities of oil must feed through the wick in three equal intervals of time of eight hours each. At the end of the test the wick must be clean, and the sides of the oil cup bright and clean.

Loss by Evaporation.—"Volatility Test."—In the case of fatty oils the point at which evaporation commences to take place almost coincides with the temperature at which decomposition occurs, whereas in the case of mineral oils, consisting as they do of oils of different boiling points, evaporation—and consequently loss to the user of the oil—may set in below the temperature at which the bulk of the mineral oil volatilises.

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[1] Daeschner (amylalcohol), German patent 124,980; Holde (petroleum ether), German patent 185,690; cp. also *Zeits. f. angew. Chem.*, 1907, 1263; Diamand, German patent 176,486; Köttnitz (ethyl acetate), German patent 191,839; and H. Kantorowicz, *Chem. Zeit.*, 1914, 38, 494. With regard to acetone, cp. Perdit and Jaguboff, *Baku Imp. Russ. Tech. Soc.*, 1906, No. 7; cp. also Charitschkoff, *Petroleum*, 1907, 99.

[2] *Journ. Soc. Chem. Ind.*, 1905, 315.

The method ordinarily adopted to determine the loss by evaporation is to heat an accurately weighed quantity on a watch glass for several hours and to weigh the residue. Oils intended for the lubrication of machinery at normal temperatures would be kept for a few hours at 100° C. Cylinder oils are heated in a drying oven or in a suitable oil-bath at temperatures varying from 150° to 300° C. The German railways prescribe for a cylinder oil intended for use with superheated steam a maximum loss of 2 per cent after two hours' heating at 300° C.

Archbutt[1] recommends as a more reliable method to heat the oil in a current of air or superheated steam. 0·5 grm. of the sample is put in a platinum tray, which is placed in a glass tube, and thus introduced into a copper tube, $\frac{7}{8}$ in. internal diameter and 2 ft. long. Round the copper is coiled a tube, $\frac{3}{8}$ in. diameter and about 10 ft. long, one end of which enters the wider copper tube and serves to heat the current of air or steam which is passed over the oil. The coiled tube is fixed in an air-bath and heated by a row of small gas jets to the desired temperature, which is controlled by a thermometer. A measured quantity of air is passed over the oil at the rate of 2 litres per minute for exactly one hour; the oil is then withdrawn and weighed. Good locomotive cylinder oils should not lose more than 0·5 per cent at a temperature of 370° F. (188° C.). The examination under this head has gained in importance since the engines using superheated steam have been introduced. *Schreiber*[2] uses another type of apparatus, fashioned upon the ordinary hot-water oven.

In the case of lubricating oils which come into contact with oxidising gases at high temperatures (*e.g.* compressed oils) the determination of the "asphaltic" bodies before and after heating will afford useful indications as to the suitability of an oil for the given purpose.

Nicolas[3] patents an apparatus for the determination of the constituents which are volatile in superheated steam.

The determination of **paraffin wax** (German, *Paraffin*) will but rarely be required. Lubricating oils containing too much paraffin wax would not prove satisfactory in the "cold-test," and would therefore be rejected at the outset.

Holde examined the processes proposed by *Pawlewski and Filemonewicz, Zaloziecki, and Höland* for the estimation of small quantities of paraffin wax,[4] and rejected them as not admitting of general application. *Holde*[5] recommends the following *modus operandi*, which is a modification of the method originally suggested and worked out by *Engler and Boehm*[1]) :—

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[1] *Journ. Soc. Chem. Ind.*, 1896, 326.

[2] *Zeits. f. angew. Chem.*, 1910, 99.

[3] English patent 21,661, 1909.

[4] Cp. Eisenlohr, *Zeits. f. angew. Chem.*, 1897, 300.

[5] *Chem. Revue*, 1897, 21. Cp. also Tanne and Oberländer, French patent 409,516; German patent 227,334.

10 to 20 c.c. of oils poor in paraffin wax (such as Russian distilled oils, solidifying below −5° C.), or 5 grms. of oils rich in paraffin wax (such as American, Scotch, Galician, etc., solidifying at or above 0° C.), are placed at the ordinary temperature in an Erlenmeyer flask of 150 to 200 c.c. capacity, and so much of a mixture consisting of equal parts of nearly absolute alcohol (98·5 per cent) and ether are added that a clear solution is obtained. The flask is then immersed in a freezing mixture at from −20° to −21° C. Whilst the solution is being vigorously agitated, so much of the alcohol-ether mixture is added that the drops of oil just disappear, and only crystals or flocks of paraffin wax are noticeable. The crystals are filtered off at the same low temperature on a cooled filter and washed with the alcohol-ether mixture, previously cooled down to −20° to −21° C., until 5 to 10 c.c. of the filtrate no longer give an oily residue. Prolonged washing beyond this point leads to loss. The paraffin wax retained on the filter is rinsed into a capsule with benzene. The solvent is then evaporated off and the residue dried at 105° C. for 15 minutes. This latter direction must, however, be used with due discretion, and prolonged heating in the air-bath must be avoided, as otherwise loss may occur ; the smell of the vapours will afford the necessary guidance.

The objections raised by *Eisenlohr*[2] against this method because of its leading to incorrect results in the case of soft paraffin waxes have been met by a modification of the original process (*Holde and Allen*[3]). For a rapid method of estimating the paraffin wax, suitable for works practice, *Charitschkoff*[4] recommends a special method. *F. Schwarz and H. von Huber*[5] use as a solvent butanone of the specific gravity 0·812.

"Deblooming" Agents.—For the purpose of artificial deblooming, **nitrobenzene** and **nitronaphthalene** are most frequently employed. Since both are soluble in dimethylsulphate, *Valenta* suggests this reagent as a means of extracting them.

Nitrobenzene is readily detected by its smell, especially on warming. It should, however, be noted that nitrobenzene is added frequently as a perfume.[6]

For the detection of *nitronaphthalene* in mineral oils, *Leonard*[7] proposes the following method, which is based on the reduction of nitronaphthalene to naphthylamine :—A small quantity of the oil is gently warmed with zinc-dust and dilute hydrochloric acid, and the mixture agitated from time to time. The fæcal odour characteristic of α-naphthylamine will then be noticed. The acid aqueous liquid is drawn off and tested in the following manner :—A portion of the liquid is neutralised with ammonia ; on adding ferric chloride a blue precipitate is obtained which rapidly becomes purple. The remainder of the liquid may be made alkaline with soda and extracted with ether. The latter is then evaporated, and the residue dissolved in a little alcohol. On the addition of a drop of a solution of sodium nitrite, which has been acidified with acetic acid, a yellow colour is produced. On adding hydrochloric acid the colour is changed to crimson. *Schulz*[1] states that by the following method 0·05 per cent of nitronaphthalene can be detected :—10 grms. of oil are heated to 290-300° C. with 0·5 grms. of colophony. When the temperature has fallen to 80° C. 4 grms. of a 10 per cent solution of sulphuric acid are added, and the mixture shaken. The flask is then allowed to settle on the boiling-water bath, the lower aqueous layer is drawn off, which on the addition of a cold saturated solution of potassium dichromate gives a blue precipitate of oxynaphthylamine.

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[1] *Dingl. Polyt. Journ.*, 1886 (262), 468.

[2] *Zeits. f. angew. Chem.*, 1897, 332.

[3] *Chem. Revue*, 1898, 112, 131 ; cp. also Clifford Richardson, *Journ. Soc. Chem. Ind.*, 1902, 690.

[4] *Chem. Revue*, 1910, 12 ; cp. also Gurwitsch, *Zeits. f. angew. Chem.*, 1910, 1306.

[5] *Petroleum*, 1913, 9, 235.

[6] Cp. French patent 365,335 (Haenflein and Kornfeld). The addition of ethereal oils, in conjunction with gum benzoin and other gums, to lubricating oils intended for internal combustion engines has been claimed by English patent 9202 (1906) ; cp. also German patent 205,883 (L. G. Leffer).

[7] *Journ. Soc. Chem. Ind.*, 1894, 69 ; cp. also Holde, *ibid.*, 1894, 906.

Many patents have been taken out for the recovery of used lubricating oils.

Examination of Greases and Solid Lubricants

The greases are conveniently subdivided into—

(α) Solidified Oils ;
(β) Rosin Greases ; Axle Greases ;
(γ) Lubricating Greases ; Lubricating Pastes.

(α) Solidified Oils

French—*Huiles solidifiées*

The solidified oils contain, as a rule, no water ; they consist preponderantly of mineral lubricating oils (of high specific gravity), which have been " solidified " or " gelatinised " by means of soda-, lime-, or aluminium-soap. The manufacture of " solidified oils " of this kind is exemplified by *Eckenberg's* patent :[2]—Fatty acids (from wool wax or crude wool fat) are dissolved in paraffin oil, and about half the amount of alkali required for the neutralisation of the free fatty acids is added. The mass is then heated so as to drive off the water and poured into moulds whilst still hot.

Lime soaps—of fatty acids or rosin acids—frequently enter into the composition of solidified oils. Waste fats (" tankage fats," cp. Chap. XVI.) are saponified with a calculated amount of lime or soda in an autoclave, and the resulting soap separated from the excess of water in a filter press. The soap, which still retains 8-10 per cent of water, is incorporated with a mineral oil. Recently a patent has been taken out for the preparation of solidified oils by emulsifying hydrocarbon oils with glue or other nitrogenous substances, and the subsequent treatment of the product with iron sulphate.[1] *Schmitt*[2] treats the fat dissolved in mineral oil with a concentrated solution of sodium aluminate.

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[1] *Chem. Zeit.*, 1909, 1093.

[2] English patent No. 16,541, 1896 ; Lecocq, French patent 439,467.

Lubricants of this kind possess sufficient consistence to be cut into lumps. "Vaseline bricks" belong to this class of solidified oils.

The analysis of these products embraces the determination of the ash, of the amount of unsaponifiable matter, and of the combined fatty and rosin acids. Each of the constituents named is then further examined.

(β) **Rosin Greases—Axle Greases**

French—*Graisses à base de résine.* German—*Wagenfette, Patentfette.*

Rosin greases are essentially solutions of calcium "rosinate"[3] in rosin oil. They are prepared by stirring dry slaked lime, freed from all gritty particles by careful sieving, into mineral oil, until a homogeneous mixture is obtained, and then adding rosin oil containing "rosin acids."

The proportions of lime and mineral oil usually taken are 5 and 95 respectively. Into this mixture ("stock") a distilled rosin oil ("set"; German—*Harzstocköl*), containing rosin oil acids (see Vol. I. Chap. IX.), is run, the mass is carefully stirred for a short time and then allowed to stand.[4] The rosin oil acids combine with the lime, and the lime soap so formed is capable of holding both the mineral oil and the rosin oil in a semi-solid emulsion. It depends on the specific gravity of the mineral oil as to whether the grease is lighter than water ("Floating Grease," "Corfe Grease"; German—*Schwimmfett*) or heavier ("Non-Floating Grease").

(γ) **Lubricating Greases—Lubricating Pastes**

French—*Graisses consistantes, graisses lubrifiantes.* German—*Consistente Fette, Starrschmieren, Zähschmieren.* Italian—*Grasse lubrificanti, grasse consistenti.*

Lubricating greases represent essentially semi-solid or solid emulsions[5] of fats, fatty oils, mineral oils, rosin oils,[6] with lime-, soda-, or zinc-soaps. They also contain a certain amount of water, the maximum reaching 35 per cent.

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[1] Armstrong, English patent 18,300, 1911.

[2] German patent 274,209.

[3] Rosinate is perhaps not the correct term, since F. Schulz (*Chem. Revue*, 1909, 186) has shown that by mixing a rosin oil freed from rosin acids with rosin, a good grease could not be obtained.

[4] *Seifensieder Zeit.*, 1910, 1071; 1911, 85, 146, 169, 233, 285.

[5] Cp. also Holde, *Zeits. f. angew. Chem.*, 1908, 2138.

[6] For cheap greases wool grease also is used. The employment of wool wax is claimed by German patents 144,465, 144,657 (Finke), and 188,712 (Siemsen); cp. "Emulsified Oils" (below).

These lubricants are prepared by dissolving fatty oils and fats or fatty acids in mineral oil and boiling with a solution of caustic soda or with milk of lime or zinc oxide. For lubrication of hot bearings which do not come into contact with water, a grease prepared from a soda soap is almost exclusively employed, whereas those bearings which come into contact with water or steam require a grease in which lime soaps preponderate.[1] The quantity of base taken is insufficient to completely saponify the neutral fats.

If it be desired to have only a small quantity of water in the finished product, as is necessary in the case of a grease containing a considerable quantity of lime soap, a mixture of dry slaked lime and mineral oil is prepared first (as described above, p. 97), and after adding a small quantity of water, the fats, or fatty oils, or fatty acids are introduced and then partially converted into lime soaps by heating. Solidification of the lime-mineral oil "stock" may be effected at somewhat lower temperatures by introducing rosin oil containing rosin acids. The mineral oil may be replaced by anthracene oil.

Another mode of manufacturing these lubricants consists in simply dissolving a finished soda soap in mineral oil, or in mixing together oleic acid, mineral oil, and the requisite quantity of a solution of caustic potash or soda. In order to thicken the mixture, *aluminium oleate* is introduced together with the soda soap. If a lead soap[2] be used the so-called *galena oils* are obtained. A grease prepared by mixing castor oil with sodium silicate and a filler is stated to resist the action of petrol.[3]

To these greases are also added inert substances, such as talcum, powdered mica, plumbago,[4] or cork,[5] with a view to increasing their lubricating power. Therefore the talcum, mica, plumbago, and cork cannot be looked upon as adulterants.[6] It should, however, be understood that these substances are not lubricants, but merely exercise an apparently beneficial influence in that they act as abrasive material, helping to grind down uneven surfaces, and further in that they fill up minute grooves in the bearings. For a comparison of oils with and without graphite, the reader must be referred to the original paper by *Mabery*.[7]

Thomsen[8] differentiates between graphite and other forms of carbon by means of the specific gravity. Graphite having a specific gravity of about 2·2 can be separated from amorphous carbon, which has a specific gravity under 2·0, by means of ethylene bromide, of a specific

[1] Kragenski, *Seifensieder Zeit.*, 1913, 266.

[2] Lead soaps of rape oil (obtained by saponification with lead oxide), emulsified with water, used to be employed in the fifties and sixties of the last century as railway waggon greases, notably in Germany (cp. Grossmann, 1909, 4).

[3] A. G. Hopkins, *Eng. Pat.*, 116, 1915.

[4] Cp. German patent 189,950 (Knowles and Chapman); United States patents 843,426 and 844,989; German patents 191,840, 218,218 (E. G. Acheson); German patent 140,882 (W. F. Downs); English patent 23,622 (B. L. Philips-Smith).

[5] A. Stiewing, German patent 246,582.

[6] Downs (German patent 140,882) patents the employment of castor oil as a binding agent for lubricants of this kind.

[7] *Journ. Ind. and Eng. Chem.*, 1910, 115. Cp. also Memorandum on Solid Lubricants, *Bulletin*, No. 4.

[8] *Ibid.*, 1911, 871.

gravity 2·15. For the detection of graphite in the presence of other forms of amorphous carbon, *Marcusson and Meyerheim*[1] propose the following method :—1 grm. of the benzol extracted residue is introduced in small quantities into 15 grms. of molten caustic potash contained in a nickel crucible. The mass is fused for 15 minutes over a flame and finally over a blow-pipe. It is then dissolved in water, and the insoluble residue washed by decantation. The insoluble graphite is washed with dilute hydrochloric acid, and finally in water, dried at 105° C. and weighed. These observers state that different forms of graphite yield different amounts of insoluble matter, and therefore their method is only approximate.

Frequently greases of this kind are perfumed with mirbane oil, and coloured yellow with aniline dyes or annatto.

The specification of the London County Council of a light grease for electric cars requires a grease in which the loss, when dried at 200° F., shall not exceed 5 per cent, and the mineral matter not to exceed 4 per cent. The same authority specifies for *Stauffer's* lubricant that it should not contain more than 2 per cent of free acid as oleic acid, and that the loss at 212° F. shall not exceed 3 per cent.

Special kinds of this class of greases are those known as *Stauffer's lubricants*, *Tovote greases*, etc.

To this class of lubricants belong also railway waggon greases. These are generally prepared by melting together tallow and palm oil at a temperature of about 100° C., running into the melted fat a solution of sodium carbonate, previously heated to the same temperature, and stirring the mass until it solidifies. Since palm oil contains a considerable amount of free fatty acids, palm oil soap is formed, which holds the unsaponified part of the palm oil and the unsaponified tallow in solid emulsion.

The machinery required for the manufacture of lubricating greases is of the simplest description. The mixing of the ingredients by hand is still frequently resorted to. Simple machinery consists of a revolving barrel turned by a handle. In more modern installations, intended for large scale manufacture, the ingredients are boiled together in large jacketed pans, fitted with stirring gear, so that all the mixing required can be done in one vessel. In the case of more complicated greases the preparation of the soap is carried out in a separate vessel, and the intermixing of the other ingredients with it is performed in a second vessel. In order to prevent hard lumps of lime soap, or even soda soap, remaining in the finished grease, the product is run through a finely meshed sieve ; in some cases, especially when the grease is very viscous, it is passed through a kneading machine (mostly consisting of a pair of rollers) which imparts to the finished grease homogeneity and a soft texture and also some lustre. These machines are similar to those mentioned under " Vegetable Butter."

An important point is that the lubricating greases should not separate, on keeping, into an oily and into a solid substance.

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[1] *Chem. Revue*, 1911, 144.

In the examination of lubricating greases the determination of the melting point is frequently of importance. This may be done by *Pohl's* or by *Ubbelohde's* method (Chap. V.), or by placing 50 to 100 grms. in a wide test-tube, such as is used for the titer test determination, inserting a thermometer in the grease, and placing the test-tube in a water-bath or a sulphuric acid bath and observing the temperature at which the mass is completely melted. In the last case stirring of the mass is essential, so as to prevent liquation or exudation of the oils or oily substances from the soaps. Naturally the melting point will extend over a range of several degrees; the indications thus obtained are, however, sufficiently accurate for most practical purposes, as it is merely required to know whether the grease will "flow" within certain degrees of temperature. *Gillett* recommends the determination of the consistence by means of *Legler's* apparatus (Vol. I. p. 369).

The compositions of most of these lubricating greases are guarded by their manufacturers as valuable secrets. Each grease requires, therefore, a special method of analysis. The chemical examination comprises the determination of the following constituents:—1. Water; 2. Fatty acids and (or) rosin acid combined as soap[1] (free fatty acids, if any); 3. Unsaponifiable matter; 4. Unsaponified fat; 5. Ash. Each of the constituents named under Nos. 2, 3, and 4 must be further examined according to the methods detailed in Vol. I. Chapters V.-X., and on the foregoing pages.

The lubricant is first dried at 100° C. and the amount of water is thus found, provided volatile hydrocarbons or ethereal oils be absent (cp. p. 89). At the same time the anhydrous lubricant is obtained in a proper form for subsequent examination. The residue is next extracted with a suitable volatile solvent, when added mineral matters—weighting substances—and practically the total amount of soaps remain undissolved, whereas the unsaponifiable matter and the unsaponified fat (and free fatty acids if any) pass into solution. According to *Marcusson*[2] acetone is the best solvent for this purpose, as it dissolves less of the soaps than petroleum ether. The undissolved portion is examined for soluble (soda) soap by boiling out with water; if insoluble soaps be present, recourse must be had to the method described under "Metallic Soaps" (see below). The solvent is evaporated off from the dissolved portion, and the residue so obtained is boiled with alcoholic potash. The unsaponifiable matter is then determined, and examined by the methods detailed in Vol. I. Chap. IX. The fatty acids and rosin acids liberated from the soap solution may then be further examined. The chemical analysis gives, however, no definite information as to the lubricating value.

Hot neck Greases (see under "Candle Manufacture").

Stuffing Greases (see Chap. XVI.).

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[1] Cp. Marcusson, *Chem. Revue*, 1913, 43.

[2] *Seifensieder Zeit.*, 1913, 1417. Cp. also J. Marcusson and H. Smelkus, *Petroleum*, 1921, 17, 818.

III. Mechanical Tests

The physical and chemical examinations described above by no means exhaust the tests to which a lubricating oil must be submitted in order to arrive at a definite opinion as regards its suitability for a given purpose. It may therefore be useful to point out once more that the determination of the viscosity does not furnish a complete answer as to the lubricating value of a given oil, for a substance may be viscous and yet not be a good lubricant, as not having the " body " or " oiliness " (French—*corps liant*; German—*Schlüpfrigkeit*) which shows itself by the " smoothness " felt when the oil is rubbed between the fingers. On the " smoothness " or " oiliness " depends the thickness of the oil-film which a lubricant forms when applied to running machinery. " Smoothness " or " oiliness " depends on the nature of the oil, and is greatly affected by the pressure, speed of the running machinery, and also by the temperature to which the lubricant is exposed.

It is impossible to ascertain the behaviour of a given oil in these respects by means of the physical and chemical examinations described above. Hence they must be supplemented by mechanical tests.

Railway Companies and other large consumers of lubricants test the lubricating power of these by means of specially designed apparatus, " oil-testing machines," simulating as nearly as possible the conditions obtaining in practice.

A considerable number of mechanical oil-testing machines have been described and patented. Since this subject necessarily falls outside the scope of this work, the reader is referred to the sources given in the footnote.[1] It should, however, be noted that opinions arrived at on the strength of tests carried out by means of oil-testing machines are not always confirmed by practice. For although the best oil-testing machines, if attended to properly, furnish comparable results, these do not depend solely on the properties of the lubricant, but to a considerable extent also on the material of the bearings and on the condition of the latter. Moreover, a great deal depends on the manner in which a lubricating oil is applied. At present, when " pressure " lubrication is substituted for " drip " lubrication, the construction of the bearings is entirely different from that used in testing machines.

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[1] B. Tower, *Proc. Inst. Mech. Eng.*, 1883–1891; C. J. H. Woodbury, *Measurements of the Friction of Lubricating Oils*, New York, 1885; Redwood, *Journ. Soc. Chem. Ind.*, 1886, 121; Carpenter-Leask, *Soaps and Candles*, pp. 258-313; Thorpe's *Dictionary of Applied Chemistry*, vol. ii. p. 474; Thurston, *Treatise on Friction and Lubrication*, pp. 248-263; B. Redwood, *Petroleum*, p. 634; Goodman, *Recent Researches in Friction*; *Proc. Inst. Civil Engineers*, vol. 85; Petroff, *Neue Theorie der Reibung*, Hamburg, 1887; Archbutt and Deeley, *Lubrication and Lubricants*, p. 319; Holde, *Die Untersuchung der Schmiermittel*, p. 224; Weiss, *Dingl. Polyt. Journ.*, 1898 (309), 76; H. V. Blake, English patent 25,492 1902; K. Wilkens, English patent 20,998, 1902; English patent 15,897, 1902 (Dettmar's Oil-Testing Apparatus; cp. *Chem. Zeit.*, 1906, 155, 306); Kirsch, *Mitt. d. K. K. Technolog. Gewerbe Museums*, 1906, xvi. No. 1; Mabery and Mathews, *Journ. Amer. Chem. Soc.*, 1908, 992; W. Lees, T. W. Lees, and A. Lees, English patent 27,036, 1906; Grossmann, *Die Schmiermittel*, Wiesbaden, 1909; H. Benjamin, cp. Sibley, *Journ. Amer. Soc. Mech. Eng.*, 1909, 1099; Alexander, *The Engineer*, 1909, 291; Kapff, German patent 209,399; Conradson, *Journ. Ind. Eng. Chem.*, 1910, 171; Drosten, German patent 275,225; Schmitz, *Zeits. f. angew. Chem.*, 1914, 468; H. K. Moore and G. A. Richter, *Met. and Chem. Eng.*, 1917, 16,692; R. Hislop, English patent 29086.

An apparatus for testing the behaviour of lubricating oils in the presence of steam or hot gases has been patented by the *Olwerke Stern-Sonneborn A.G.*[1]

V.—WOOL OILS—CLOTH OILS [2]

French—*Huiles d'ensimage.* German—*Wollspicköle, Wollschmalzöle, Wollöle.* Italian—*Olii da filatura.*

Under the trade term " wool oils " or " cloth oils " are comprised all those oils that are used by woollen manufacturers for lubricating the wool before spinning, or for oiling the rags before grinding and pulling.

The best wool oils consist of pure fatty oils, such as olive oil, lard oil, neat's foot oil. Besides these, oleic acid (" saponification oleine " or " saponified oleine," " distillation oleine " or " distilled oleine," see below) is used largely as a cheaper kind of wool oil. It commends itself also for the reason that it is easily removable in the scouring process ; still, it should not be used for the finest goods, as the action of the fatty acid on the metal of the scribblers is apt to cause defects in the woven goods.[3] The tendency to produce cheap wool oils, especially those for use with the lowest textile goods, has led to the employment of " distilled grease oleine " (see Chap. XVI.), and even " waste oils," such as " black recovered oil," " seek oil," and " brown grease oil " (cp. " Waste Fats," Chap. XVI.). The last-named oils contain considerable amounts of unsaponifiable matter. Besides these oils there are found in commerce large quantities of " manufactured oils," representing blends of the above-named wool oils, as also blends containing mineral oils. The principles upon which the valuation of wool oils should be based are the following :—

(1) Wool oils should be *easily removable in the scouring process.* They should therefore be free from drying and semi-drying oils or their fatty acids, as also from rosin acids and rosin oils, since all these substances offer great resistance to removal in the scouring process, become sticky, leave an unpleasant odour on the fabric, and cause stains in the finished cloth. For the best goods even small quantities of hydrocarbons in the oils are objectionable, as, in addition to other disadvantages, they cause faults in the dyeing of the finished cloth. The determination of the ash is also of importance, since the deposition of the insoluble salts of iron and lime with fatty acids on the fabric hinders the bleaching.[4]

Although mineral oils readily form emulsions with soap solutions, practical experience shows that they are not so easily removable as their behaviour with soap solutions might lead to anticipate, and that they actually militate against the obtaining of properly bleached goods. Therefore, for best goods wholly saponifiable wool oils only should be used. The low class wool oils containing large proportions of hydrocarbons can only be removed by the employment of strongly alkaline soaps.[1]

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[1] English patent 7616 and 7617, 1911 ; German patent 232, 233 ; French patent 413,996.

[2] Cp. Lewkowitsch, *Journ. Soc. Dyers and Colourists,* 1896, 60 ; *Journ. Soc. Chem. Ind.,* 1896, 459.

[3] " Ricinoleic " acid (castor oil fatty acid) has also been recommended as a wool oil (Crosfield and Markel, English patent 9946, 1904). The advantage claimed over oleic acid is that the castor oil acids do not solidify so readily as does the former at low temperatures.

[4] Klemm, *Zeits. f. angew. Chem.,* 1912, 30 ; cp. also Scheurer, *Bull. Soc. Ind. de Mulhouse,* 1910, 343.

(2) Wool oils should *develop as little heat as possible* both in the stored raw material and during the working of the oiled material. *Drying and even semi-drying oils* easily give rise to a development of heat sufficient to cause spontaneous combustion or to produce heat in the scribbling and carding process.

(3) The liability of oils *to favour the spreading of fire* should be as small as possible. Since the Fire Insurance Offices put great strictures on the users of wool oils, and assess the insurance premiums according to the quality of the oils employed, it may be found useful to quote the order in which the oils are arranged in the schedules of the Fire Insurance Companies in this country :—

A. *Free from any extra charge are*—Olive (Gallipoli) oil, lard oil, oleine (" saponified " or " distilled ") not containing more than 10 per cent of unsaponifiable matter, fish oil, or a manufactured oil (" purified by distillation or saponification," whatever this may mean) containing not more than 30 per cent of unsaponifiable matter,[2] and having a flash point not under 340° F. (167·8° C.).

B. *A higher rate* (5 *shillings extra*) *is charged for*—Manufactured oils containing more than 30 per cent, but not more than 50 per cent, of unsaponifiable matter.

C. *A still higher rate* (7½ *shillings extra*) *is charged for*—Black (recovered) oil (Chap. XVI.), not prepared or purified by saponification or distillation, or any other oil not included in A or D, or any composition containing them or any of them and not containing more than 50 per cent of unsaponifiable matter.

D. *The highest rate* (21 *shillings*) *is charged for*—Manufactured oils containing more than 50 per cent of unsaponifiable matter, or any mineral oil, oil of pine, linseed oil, rape oil, cotton seed oil, or any other seed oil.

Neat's foot oil and tallow oil are not mentioned in these schedules, although they are very useful wool oils and quite harmless, whereas, curiously enough, fish oil, which is a very dangerous oil (since cotton rags oiled with fish oil will ignite spontaneously), is permitted free of extra charge. True, cotton seed oil, which is equally dangerous, is rightly placed amongst the oils charged at the highest rate, but it is unintelligible why " oil of pine " is classed amongst wool oils (cp. also table, p. 110).

Mineral oils in themselves are not liable to spontaneous combustion ; experience shows, however, that once a fire has broken out, they assist the rapid spreading of it. For this reason strictures are laid on the use of oils containing high proportions of mineral oils.

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[1] Cp. Lewkowitsch, *Journ. Soc. Dyers and Colourists*, 1894, March ; *Journ. Soc. Chem. Ind.*, 1894, 258 ; *Journ. Soc. Dyers and Colourists*, 1896, 60 ; *Journ. Soc. Chem. Ind.*, 1896, 459 ; Spennrath and Walther, *Journ. Soc. Chem. Ind.*, 1895, 362 ; Ulrich, *Seifensieder Zeit.*, 1903, 688.

[2] The Austrian Fire Insurance Companies allow only 15 per cent of unsaponifiable matter.

Therefore *the determination of the unsaponifiable matter and of the flash point* is of the greatest importance in the analysis of wool oils.

The examination of wool oils comprises the test for purity, including the determination of the unsaponifiable matter. Some analysts ascertain the saponifiable matter only, *i.e.* the sum of the neutral fat and fatty acids, by boiling the sample with alcoholic potash (Chap. VI.), and calculating the amount of potassium hydrate (KOH) used to oleic acid, thus obtaining the "unsaponifiable matter" by difference.[1] This method must be rejected as leading to erroneous results in many cases; the unsaponifiable matter should be determined direct by extraction with a solvent (Vol. I. Chap. IX.).[2]

Another error committed by some analysts is to return the "unsaponifiable matter" as mineral oil, a misnomer which may lead to considerable loss to the user of the oil. The unsaponifiable matter should only be returned as mineral oil when the detailed examination warrants such a statement. Even if the unsaponifiable matter be liquid or fluorescent (cp. Chap. XVI., "Distilled Grease"), it must not be judged to consist of mineral oils, as the hydrocarbons formed by destructive distillation of wool fat[1] have the same appearance. In case wool fat hydrocarbons be present, they will show the isocholesterol reaction (Chap. III.). It should be noted that since the Fire Insurance Offices fix their rates according to the amount of unsaponifiable matter, *rosin* is now added fraudulently. This is detected and determined in the saponifiable part (*i.e.* soap solution) as described in Vol. I. Chap. X.

The liability of an oil to "gum" after exposure on the fibre may be approximately determined according to *Gill and Shippe*[3] by observing the increase in viscosity after heating the oil exposed in a thin layer to a current of air.

The determination of the flash point is carried out as described, p. 77. The flash point of a wool oil should not be below 170° C. (340° F.).

A rapid method of determining the relative liability of wool oils to spontaneous combustion is afforded by using *Mackey's* "Cloth Oil Tester."

This apparatus (Fig. 7) consists essentially of a cylindrical metal water-bath, provided with a lid having a nozzle for inserting a thermometer, and fitted with two tubes A and B for air currents which pass through the cylinder in the directions of the arrows. Inside the apparatus is placed a cylinder C of wire gauze, containing a ball of cotton wool oiled with the sample under examination. To perform the test weigh out 14 grms. of the sample into a shallow dish containing 7 grms. of clean cotton wool.[4] Tease out carefully the cotton wool by hand, so that the oil is thoroughly distributed throughout the mass. This teasing and incorporation of the oil with the cotton must be done with the greatest care, as the success of the experiment depends on the even distribution of the oil. Transfer the oiled cotton wool to the cylindrical cage C, holding the thermometer in its place, whilst the cotton wool is being packed around it. Bring the water in the jacket to vigorous boiling, place the cage in the air-bath, slip the lid down over the stem of the thermometer, and fix it in its place [1] by means of the clamp D. Keep the water in the bath boiling, and note the temperature after the lapse of one hour. Care must be taken that no moisture enters the air-bath.

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[1] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 142. The importance of this question with regard to insurance risk has been clearly stated in a paper by Mackey, read before the Insurance Institute of Yorkshire. Cp. *The Textile Manufacturer*, 1894, 18.

[2] The determination of free fatty acids is of minor importance. Cp., however, Richardson and Jaffé, *Journ. Soc. Chem. Ind.*, 1905, 534.

[3] *Journ. Ind. Eng. Chem.*, 1911, 72.

[4] For comparative tests using cotton wool, wool, slag wool, and glass wool, see W. M'D. Mackey, *Journ. Soc. Chem. Ind.*, 1915, 595.

If the thermometer registers over 100° C. at the end of the first hour, the oil under examination must be considered as dangerous. In the case of very dangerous oils the temperature will run up to 200° C. within one hour and a half. Should the temperature rise very rapidly above 150° C., it is best to withdraw the thermometer, as the oiled cotton wool may ignite.

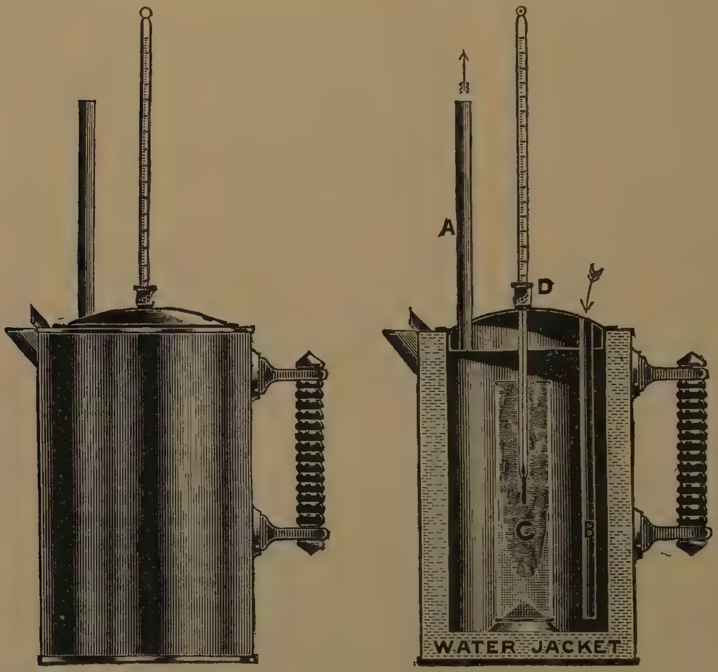

Fig. 7.

The following table contains the results of a number of experiments carried out by *Mackey*: [2]

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[1] The thermometer provided with the apparatus bears a red mark on the stem; it should be so fixed that the red mark is just visible. The apparatus is supplied by Reynolds and Branson, Leeds.

[2] *Journ. Soc. Chem. Ind.*, 1896, 90. Similar but very rough experiments were made before him by *Gellatly* (1874) to test the liability to spontaneous combustion of lubricating oils. Cp. also Kissling, *Journ. Soc. Chem. Ind.*, 1895, 479.

No.	Substance.	Temperature in 1 hr.	Temperature in 1 hr. 15 m.	Temperature in 1 hr. 30 m.	Temperature in 2 hrs.	Maximum.		
		°C. = °F.	°C. = °F.	°C. = °F.	°C. = °F.	°C. = °F.	H.	M.
1	Cotton seed oil[1]	125=257	242=468	.. ..	.. ..	242=468	1	1
2	,, ,,	121=250	242=468	282=540	.. ..	284=543	1	35
3	,, ,,	128=262	212=414	225=437	.. ..	225=437	1	30
4	,, ,,	124=255	210=410	.. ..	.. ..	248=478	1	35
5	,, ,,	116=241	192=378	200=392	.. ..	200=392	1	30
6	,, ,,	118=244	191=376	202=396	.. ..	202=396	1	30
7	,, ,,	117=243	190=374	194=381	.. ..	194=381	1	30
8	,, ,,	112=234	177=351	204=399	.. ..	211=412	1	45
9	Olive oil fatty acids	114=237	177=351	.. ..	.. ..	196=385	1	25
10	,, ,,	105=221	165=329	.. ..	.. ..	293=559	1	55
11	,, ,,	102=216	135=275	208=406	.. ..	226=439	1	45
12	White Australian Oleine	103=217	115=239	191=376	.. ..	230=446	1	45
13	Olive oil (containing 1% free fatty acids)	98=208	102=216	104=219	.. ..	241=466	3	25
14	Oleine	98=208	101=214	102=216	.. ..	110=230	2	8
15	97% Oleine	98=208	100=212	102=216	.. ..	172=342	3	15
16	Belgian Oleine	98=208	99=210	100=212	.. ..	173=343	3	16
17	Olive oil (neutral)	98=208	100=212	101=214	.. ..	235=455	5	15
18	,, ,,	97=207	100=212	101=214	.. ..	228=442	4	30
19	,, ,,	97=207	.. ..	101=214	.. ..	235=455	4	55
20	Cotton seed oil	139=282	.. ..	.. ..	.. ..	200=392	1	4
21	Olive oil	99=210	101=214	102=216	103=217	113=235	4	30
22	Mixture of 50% of No. 20 and 50% of No. 21	102=216	117=243	.. ..	.. ..	200=392	1	29
23	,, 25 ,, ,, 75 ,,	99=210	105=221	112=234	.. ..	200=392	1	52
24	,, 10 ,, ,, 90 ,,	99=210	102=216	105=221	127=261	200=392	2	9

The method described being a comparative one,[2] the directions given must be strictly followed. It will be found useful, before examining a sample, to test pure olive and cotton seed oils as representatives of a safe oil and a dangerous oil respectively.

The author has worked very extensively with this "Cloth Oil Tester," and can recommend it as being a very useful instrument. Less simple is the apparatus described by *Richards*.[3] This consists of an outer shell formed by a 6-inch wrought-iron tube, closed at each end by a removable disc of wood. Into this tube is inserted an inner 4-inch tube of sheet-iron, with an overlapping metal cover at each end. Thus there is left an air space of 1 inch round the inner tube and of 3 inches at each end. The apparatus is placed on a tripod and heated by a Bunsen burner. Three thermometers, which are inserted into the inner shell through the outer one, allow the temperature to be read off.

To test an oil, 50 grms. are evenly distributed over 50 grms. of cotton waste; the waste is carefully pushed into one end of the inner tube, and a thermometer inserted into the middle of the ball. A second ball of unoiled waste is placed similarly at the other end of the tube. On heating, the thermometer inserted into the blank waste should not rise above 100°-101° C.; this can be easily controlled by the reading of the middle thermometer. The latter should be kept at about 125° C. The results obtained with this apparatus are stated to have been useful for ascertaining the cause of fires and for gauging the degree of safety of oils. Furthermore, the percentage of fatty oil which may be safely mixed with mineral oil was thus determined. The experiments showed that neat's foot oil and best lard oil may be mixed with mineral oil to the extent of 50-60 per cent of the latter, while in the case of cotton seed oil the limit of safety was reached at 25 per cent.

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[1] Linseed oil and also maize oil would, of course, "fire" much sooner.

[2] In order to obtain more uniform results, Archbutt (*Journ. Soc. Chem. Ind.*, 1899, 347) recommends the passing of a regulated current of air, two litres per minute, through the apparatus (Fig. 7) down the tube B.

[3] *Journ. Soc. Chem. Ind.*, 1892, 547. The apparatus is also known as *Ordways*; cp. also Dennstedt, *Berichte*, 1911, 20.

Gill[1] proposed a modified *Ordway*[2] apparatus by using a 4-inch jacketed tube. The jacket is filled with water and heated by a flame until 15 lbs. pressure is marked, so that the blank waste attains a temperature of 100° C. The cotton waste is confined in wire gauze cages, and after the temperature has reached 125° C. a blast of air at a pressure of 7 lbs. is blown through the apparatus at the rate of 0·4 cubic feet per minute. The results obtained by the three apparatus are shown in the following table :—

Comparison of the Various Apparatus for the Spontaneous Combustion Test of Oils

Oil.	Mackey Apparatus.		Ordway Apparatus.		Gill's Apparatus.	
	Temp.	Time.	Temp.	Time.	Temp.	Time.
	°C.	Mins.	°C.	Mins.	°C.	Mins.
Olive, containing 5·3 per cent of free fatty acid; iodine value 85·4	234[3]	130	222	180	186	205
	230	130	150	300	196	190
					221	260
Lard, containing trace of free fatty acid; of iodine value 75·2 .	234[3]	80	200	150	192	185
	234	75	215	290	197	230
					220	220
Oleine . . .	...	...	178[4]	165	195	360
Oleic acid of iodine value 60·5 . .	113	150	178	120	...	...
	158	188	275	190	...	...
Cotton seed, practically neutral; iodine value 108·9 . . .	234[3]	70	186	135	200	225
	234[3]	75	200	280	198	265
Linseed, practically neutral; iodine value 168·1 . . .	234	65	160	120	201	165
	234	75	218	240	192	130
25° Paraffin; iodine value 16·2 . .	97	135	...	...	102	280

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[1] *Journ. Soc. Chem. Ind.*, 1907, 185.

[2] *Ibid.*, 1892, 547. The apparatus is also described as *Richards'*.

[3] This was as high as the thermometer furnished with the apparatus would indicate; other temperatures represent the maximum temperature attained.

[4] Not the same sample as the others. Other figures were: 200° in 150 minutes, 174° in 180 minutes, 201° in 195 minutes.

It will be seen that *Mackey's* apparatus gives the most concordant results in the shortest time.

In the following table are collated a few analyses of some distilled oleines from "recovered grease," which are used as wool oils :—

Wool Oils—Distilled Oleines from Recovered Grease[1]

Flash Point.	Specific Gravity at 15·5° C.	Free Fatty Acids.	Unsaponifiable.	Neutral Wax.	Observer.
°F.		Per cent.	Per cent.	Per cent.	
...	0·8894	77·2[2]	26·8	...	Allen
...	0·9083	55·3[2]	35·9	11·6	,,
...	...	54·9[3]	34·5	11·28[4]	Lewkowitsch
338	0·9031	55·02	34·66	...	Hurst
342	0·8980	56·26	29·46	...	,,
322	0·9050	53·65	16·32	...	,,
...	0·9000	59·83	38·92	...	,,
...	0·9091	64·42	9·95	...	,,
415	0·941	...	41·7	...	Hess
...	0·9060 at 15°	41·5[5]	57·7[6]	...	Marcusson[7]

A few analyses, due to *Mackey*, of low-class wool oils are collated in the following table :—

Description.	Flash Point.	Moisture.	Unsaponifiable.
	°F.	Per cent.	Per cent.
Brown oleine, compound oil of English distilled and foreign oils	396	0·77	12·95
Brown foreign oleine, Belgian	354	0·75	18·69
Brown "oleine cloth oil," "manufactured" .	349	0·64	25·58
"Black oil," recovered after using foreign and English distilled oleines (flannel district, Lancashire)	367	1·27	29·65
"Brown grease," recovered after using Gallipoli oil	419	1·07	29·77
Distilled oleine from brown grease and once recovered olive oil	342	0·77	37·19
"Black oil," recovered after using oleine and better class "cloth oils" (half "seek,"[8] half waste)	369	1·11	38·50
Brown oleine, distilled from brown grease .	338	0·69	52·35
"Black oil," recovered after using recovered and low cloth oils (from waste)	331	0·67	67·30
"Brown pulling oil" (for rags), brown grease and hydrocarbons	374	0·74	78·25

A more complete series of analyses of some commercial wool oils carried out by the author is given in the following table :—

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[1] Cp. Vol. I. Chap. XI. and Vol. III. Chap. XVI.

[2] Calculated as oleic acid.

[3] Mean molecular weight 286.

[4] Consisting of 7·02 per cent of fatty acids and 4·26 per cent of combined alcohols.

[5] Iodine value 35·2, mean molecular weight 276.

[6] Consisting of 52·7 per cent of hydrocarbons and 5 per cent of alcohols.

[7] *Mitt. Königl. Vers. Anstalt*, Berlin, 1903, 48.

[8] Cp. Chap. XVI. "Seek Oil."

Analyses of some "Wool Oils" (Lewkowitsch)

	Ratings by English Fire Insurance Companies.								
	Class A.	Class A.	Class B.	Class B.	Class B.	Class C.	Class C.	Class C.	Class D. Rape Oil.
Specific gravity at 60° F.	0·9208	0·9048	0·9016	0·9000	0·9019	0·9064	0·9140	0·9112	...
Free fatty acids, as oleic acid	39·6%	58·7%	32·4%	51·1%	52·2%	51·9%	41·20%	31·58%	...
Saponification value	148·2	123·2	68·88	107·9	116·6	113·7	103·9	91·29	...
Unsaponifiable	26·97%	41·88%	67·39%	48·97%	44·5%	45·41%	41·14%	56·35%	...
Flash point—Close test	333° F.	326° F.	326° F.	310° F.	318° F.	350° F.	344° F.	345° F.	440° F.
Flash point—Open test	359° F.	348° F.	328° F.	344° F.	340° F.	364° F.	388° F.	370° F.	526° F.
Ignition point	410° F.	388° F.	376° F.	366° F.	388° F.	393° F.	410° F.	394° F.	Above 600° F.
Loss on heating for 1 hour at 340° F.	26·27%	24·89%	34·02%	23·34%	28·13%	20·42%	22·30%	25·69%	2·24%

"*Emulsion Wool Oils.*"—These are largely used on the Continent, and also in this country in the manufacture of worsted goods, the chief advantage claimed for them consisting in that they are readily removed from the fibre. They are prepared by thoroughly intermixing neutral oils and oleic acid with aqueous ammonia or an aqueous solution of sodium carbonate. Practically, they consist, therefore, of an emulsion of oil and soap solution (cp. "Emulsified Oils"). In some cases mixtures of sulphonated castor oil and oleic acid are used, neutralised with alkali.

Since many emulsion oils of this class part with the neutral oil on slight dilution with water, some manufacturers add gum or gelatin-like substances. These are detected by adding strong alcohol, which precipitates them. Also decoctions of carragheen moss, "alginic" acid, and other "emulsifiers" (see "Emulsified Oils") have been proposed for the same purpose. (Textose and Sentose.) The following table (p. 112) contains the analyses of several "emulsion wool oils":—

[TABLE

Emulsion Wool Oils

Name of Oil.	Na_2O. Per cent.	NH_3. Per cent.	Water. Per cent.	Fatty Matter. Per cent.	Fatty Acids. Per cent.	Neutral Fat. Per cent.	Unsaponifiable. Per cent.	Soda Soap Anhydrous. Per cent.	Gummy Substances. Per cent.	Observer.
...	0·91	0·32	84·45	16·16	...	...	...	...	...	Horwitz[1]
...	...	...	76·67	20·86	...	...	...	0·91	0·72[2]	Morawski
"Patent oil"	0·41	1·36	...	...	70·8[3]	8·7	6·9	...	...	Lewkowitsch
...	...	12·50	34	...	45·0	7·0	...	1·5	...	Fuchs and Schiff

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[1] *Journ. Soc. Chem. Ind.*, 1890, 937. This paper contains many errors.

[2] This substance is most likely a decoction of Carragheen moss.

[3] Calculated as oleic acid.

The "Soluble Neoline" prepared according to Patent Specification 21,976, November 17, 1893, belongs to this class of oils. From the proportions given in the specification I have calculated the following percentage composition:—

Water	56·18
Soap	8·40
Heavy paraffin oil	16·82
Potassium carbonate	4·55
Glycerin	14·05

With a view to producing emulsion wool oils which remain clear even on being strongly diluted with water, use is made of the property of dilute castor oil soap and sulphonated castor oil solutions (see p. 116) of holding neutral oils in solution. Hence a number of preparations are in the market which consist either of castor oil soap containing unsaponified castor oil [1] or oleine [2] or sulphonated castor oil,[3] completely or partly neutralised with ammonia and (or) a fixed alkali [4] (cp. "Turkey-red Oils," below). For emulsion oils prepared from castor oil soap and carbon tetrachloride and other chlorinated hydrocarbons (Vol. II. p. 22) see "Textile Soaps," below; for emulsion oils from soap solutions and wool fat cp. *Hutchinson*, English patent 15,241, 1900.

Whereas no serious objection may be raised against the preparations mentioned in the last lines, emulsion wool oils prepared from sulphonated cotton seed oil [5] or other semi-drying or drying oils, or even from sulphonated oleic acid (see "Turkey-red Oils"), cannot be considered suitable for oiling wool. Emulsion wool oils containing a considerable amount of rosin acids or rosin oil have also been patented. These preparations fall under the strictures mentioned p. 103, and need not, therefore, be considered here. With regard to emulsion oils containing mineral oils, see the following section,[6] "Emulsified Oils and Fats."

VI.—EMULSIFIED OILS AND FATS

French—*Huiles et graisses émulsionnées.* German—*Emulgierte Öle und Fette.*

Under this heading is comprised a group of widely different commercial preparations which fall only to some extent under section A of this chapter. Indeed, they include products which are dealt with as manufactured products under the sections B and C. Of necessity, some of the preparations to be mentioned have already been described in the preceding sections of this chapter (*e.g.* under the heading of "Solidified Greases" and "Emulsion Wool Oils"). It appears convenient to review all these products in this section, and to refer the reader to the subsequent sections of this chapter with regard to those constituents which must be considered later on more fully.

The characteristic feature common to all true, *i.e.* permanent, emulsions prepared from oils and fats is, that they contain notable amounts of water.[7] Mere mechanical intermixing of *refined* oils and fats with water will not produce emulsions, however intimate the contact of the fatty substances and the water may be made. After the mass has been allowed to rest a short time, separation into two layers will take place. The oils and fats separating on the top retain only traces of water, and they do not exhibit the characteristic properties of an emulsion.

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[1] Cp. English patent 7231, 1905 (Riep and Bauer).

[2] English patent 7491, 1901 (Sella).

[3] German patents 113,433, 126,541, 159,220, 169,930 (Stockhausen).

[4] English patent 23,768, 1906 (Common and The Hull Oil Manufacturing Company).

[5] English patent 24,135, 1906 (Ermen).

[6] Cp. also English patent 13,580, 1905 (Fell; from E. Korndoerfer).

[7] Here it is intended to deal with true emulsions only; in a wider sense ointments and salves made up from oils and fats may also be termed "solid emulsions," but they fall outside the scope of this work. With regard to cod liver oil emulsion, cp. p. 65.

Apparatus for the production of emulsions has been patented by *Schröder*[1] and also by *Sheans*.[2]

In order to produce an emulsion, it is essential to introduce into the mixture of oils (and fats) and water a foreign substance, however small its quantity be. Such substances act as emulsifying agents, and are therefore termed "emulsifiers." The important part which emulsification plays in the practice of the oil and fat industries has been pointed out in Vol. I. Chap. II. of this work. Further theoretical[3] considerations on the nature of emulsions fall outside the scope of this work, as only the practical aspect of the question with regard to oils, fats (and waxes) can be dealt with here. It must therefore suffice to enumerate the several emulsifying substances that are used in practice, and in connection therewith to point to those commercial products which fall under this heading.

One of the best emulsifiers for oils and fats is *milk*.[4] In the manufacture of margarine extensive use is made of milk, its employment in this industry having been naturally suggested by the mode of occurrence of butter fat, its prototype. (Therefore butter and margarine are nothing else than emulsified fats.) Another important emulsifier mentioned incidentally in the preceding pages is represented by *soap solutions*, which constitute, as it were, the binding agent in the "solidified oils" and "solid lubricants" described above.

Whereas in the last two cases the soap, being used in a concentrated solution, may appear to merely act mechanically, the true emulsifying property of soap solutions becomes more apparent in the "emulsion wool oils" (see p. 111), and is especially demonstrated by the action of soap when being used as a washing and scouring agent.

The addition of decoctions of carragheen moss,[5] of gelatine, glue, etc., assists the emulsifying action of soap as such, by introducing another colloid into the mixture, whereby the coalescence of the oily globules is prevented still more effectively.

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[1] German patent 204,061; Risberg, German patent 222,529; M'C. Lewis, *Zeits. f. Chem. u. Ind. d. Kolloide*, 1909, 211.

[2] English patent 12,700, 1906.

[3] Cp. Pickering, *Trans. Chem. Soc.*, 1907, 2001; Lewkowitsch (in discussion of this paper), *Proceedings Chem. Soc.*, 1907, 256. J. Duclaux, *Journ. Chim. phys.*, 1909 (vii.), 405; C. R. Marshall, *Pharm. Journ.*, 1909 (28), 257; Spring, *Rec. Trav. Chim. des Pays-Bas*, 1909, 12; Dounan and Potts, *Zeits. f. Kolloide*, 1910, 209; Robertson, *Zeits. Chem. Ind. Kolloide*, 1910, 7; Ostwald, *ibid.*, 1910, vi. 103; Hatschek, *ibid.*, 1910, 34, 81, and 301; 1911, 97, 159, 256; Lewis, *ibid.*, 1909, 211: Bancroft, *Journ. Phys. Chem.*, **16**, 177; Meunier and Maury, *Collegium*, 1910, 277 and 285; Bingham and White, *Journ. Amer. Chem. Soc.*, 1911, 1257; Ellis, *Zeits. f. physiol. Chem.*, 1911, 321; 1912, 321; T. R. Briggs, *Journ. Phys. Chem.*, 1915, **19**, 210; F. C. Donnan, *Journ. Soc. Chem. Ind.*, 1915, 560; G. H. Clowes, *Journ. Phys. Chem.*, 1916, **20**, 407; L. Roon and R. E. Desper, *Journ. Ind. and Eng. Chem.*, 1917, **9**, 156; W. Crockett and R. Desper, *ibid.*, 1917, 967; A. Schlaepfer, *Chem. Soc. Trans.*, 1918, 113, 522; W. C. Moore, *Journ. Amer. Chem. Soc.*, 1919, **41**, 940; H. Bechhold, L. Dede, and L. Reiner, *Kolloid Zeits.*, 1921, **28**, 6.

[4] For machinery see above, "Margarine," p. 34.

[5] The addition of formalin to such decoctions is patented by the Arabol Manufacturing Co., French patent 404,059; English patent 14,119. 1909; German patent 231,449. Cp. also J. Marcusson, *Mitt. k. Materialprüf.*, 1918, **36**, 107.

The property of soaps (soaps of fatty acids, as also soaps of rosin acids) of emulsifying not only fatty oils and fats, but also mineral oils and mixtures of the substances named, is extensively employed in the preparation of the "lubricating greases" detailed above. Notable in this respect is the emulsifying power of lime and zinc soaps.

The property of oils and fats of becoming emulsified by the action of *alkalis* must be ascribed to the production of soaps by their aid. Their formation may be due either to the neutralisation of small amounts of free fatty acids, always present to some extent in commercial oils and fats (in which case alkaline carbonates suffice to produce a thorough emulsion; cp. "Tournant Oil," Vol. II. p. 354), or (and) to the saponification of the oils and fats in the presence of caustic alkali, thus leading to local formation of soap, which envelops as yet unattacked glycerides, and, by bringing thereby free caustic alkali into more intimate contact with glycerides, produces slight hydrolysis, and subsequent neutralisation of the free fatty acids formed.[1]

The emulsified oils and fats belonging to this class occur very frequently in practice. They are prepared by dissolving the desired quantity of oils in *potash-*, or *soda-*, or *ammonia-*soaps (made from fatty acids), or in soaps of sulphurised fatty acids, or rosin acids.

Of late the tendency to produce fluids retaining in solution mineral oils, as also tar oils (especially phenols), even after a considerable amount of water has been added, has led to a considerable extension of this branch of the oil and fat industry. (Naturally the dilution with water must not be carried too far, for when the point of physical stability of the homogeneous solution is disturbed the addition of water will throw the oils out of the solution.) Lubricating oils belonging to this group, as also those wool oils which contain mineral oil or rosin oil, etc., have been described already. Further examples are the lubricants used in cutting and boring steel and iron.[2] At first aqueous soap solutions were used, much as soap solutions were frequently used as a lubricant (and are still being used in the case of new machinery, the bearings of which are not yet running true). These were found to possess the drawback, not only of causing rusting, but also of lacking sufficient "body"; therefore recourse was had to emulsification with mineral oils.[3] To this class belong also the *dust-laying oils*,[4] which consist chiefly of dilute soap solutions holding mineral or tar oils in emulsion ("westrumite," "standutin," "antistoff," and "kiton"),[5] and also those fluid emulsions which are used as *disinfectants*. The latter are mainly potash soap solutions by which cresylic acids (also carbolic acid) and neutral tar oils have been emulsified; they permit of moderate or even considerable dilution with water before the emulsified oils will separate.[1] *Donnan and Potts* [2] found by determining the amount of oil which can be emulsified with soap solutions that the sodium salts of the lower fatty acids gave no emulsion, even capric acid yielding only a very thin emulsion. The addition of montan wax to emulsions is claimed to render the emulsion of soap capable of taking up larger quantities of petroleum.[3] To this class belong also fat liquors used in tanneries (see Vol. II. p. 496), which consist of the alkali salts of sulphonated fatty acids with fatty or mineral oils.[4]

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[1] *Chem. Fab.*, Westend, United States patent 1,042,915; J. H. Smith, French patent 446,570; Petroff, French patent 452,054.

[2] Department of Scientific and Industrial Research, *Bulletin* No. 2.

[3] *Chem. Fab.*, Westend, English patent 6825, 1912.

[4] Cp. German patent 158,244. Cp. R. Heise, *Arb. a. d. K. Reichsgesundheitsamte*, 1909, xxx. 93; Wallbaum, English patents 28,178, 1910; 23,468, 1911; German patent 248,084; Calvert, Aschersleben and Jeroc, German patent 254,263; Kaliwerke, Aschersleben, English patent 3515, 1911; French patent 425,838; Raschig, *Zeits. f. angew. Chem.*, 1910, 973; Kripke, German patent 236,254; Grosser, German patent 235,593.

[5] Raschig, *Ges.-Ing.*, 1910, 703.

A very powerful emulsifying agent is obtained by the interaction of concentrated sulphuric acid with fatty oils and fats or their fatty acids. As may have been gathered from Vol. I. Chap. II., an endeavour has been made by the author to base the explanation of the rationale of the "sulphuric acid saponification" on the action of the emulsifier: *sulpho-compound of the fats and oils or of their fatty acids.*

Nearly related to these sulpho-compounds, if not identical with them, are the "*sulphonated oils*" [5] (see below), a typical representative of which is Turkey-red oil.[6] The emulsifying properties of these sulphonated oils are also made use of in the preparation of some "wool oils" and of "sheep dips."

The "*Twitchell reagent*" represents a sulpho-aromatic compound possessing an extraordinary emulsifying power. The author has shown (Chap. II.) that emulsifiers, similar in composition to the sulpho-aromatic compound of benzene and oleic acid, and made with the aid of naphthalene, anthracene, and phenanthrene, have equally strong or only slightly inferior emulsifying properties.

In a lesser degree than sulphonated oils, but still to a very notable extent, *oxidised oils and fats* possess the property of acting as emulsifiers. This property is most pronounced in the oxidised oils derived from fish and blubber oils. Indeed, all the preparations described under the headings "Dégras" and "Stuffing Greases," Chap. XVI., are practically semi-solid emulsions; they seem to owe their property, viz. to remain permanent emulsions, to those oxidised oils and fats which are formed in the process of making "dégras." [7] Emulsions prepared with the aid of oxidised oils have been claimed as advantageous for the manufacture of paints by *Parrot.*[8]

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[1] Albert and Berend, German patent 250,275; Wallbaum, German patent 248,793.

[2] *Zeits. f. chem. Ind. Kolloide,* 1910, 208.

[3] Cassel, English patent 14,844, 1910.

[4] Thuau, *Collegium,* 1913, 219; Kramer, *Chem. Revue,* 1910, 1303.

[5] Laroche et Juillard, French patent 401,704; English patent 17,655, 1909. Cp. also L. Levinstein, English patents 16,577 and 16,578, 1913.

[6] Cp. German patents 166,935 (Kunick); 197,400 (C. H. Meyer); 204,906 (F. W. Klever); English patent 16,969, 1907 (L. E. Common and Hull Oil Manufacturing Co.); Arledter, English patent 12,037, 1911; F. Erban, *Zeits. f. angew. Chem.*, 1909, 55.

[7] Cp. German patent 195,410 (J. Lund); English patent 11,121, 1908; French patent 390,497; German patent 206,305 (Imbert) and German patent 204,906, being addition to German patent 174,906; cp. also under "Derivatives of Fatty Acids."

[8] French patent 373,904 (void for non-payment of fees, see *Chem. Zeit.*, 1912, 1062); Possanner, *Papier-Zeit.*, 1910, 3016, United States patent 757,948.

Special advantages have been claimed for the *amides of higher fatty acids*.[1] According to *Siemsen*,[2] there can be produced, with the aid of the amides of oleic acid and stearic acid, as also of the acidyl derivatives of organic bases (such as stearo-anilide, ricinoleic anilide, stearo-toluidide, stearo-xylidide, etc.), oil and fat emulsions which may contain any desired proportion of water. To prepare them the amides are boiled up with water, and the oils and fats are gradually introduced; at the same time a small quantity of alkali salts of higher fatty acids is added. (It would thus appear that the presence of soap is required.) The emulsions so obtained are stated to be free from the drawback which attaches to emulsions made with the aid of soap only, viz. that of separating into two layers on being warmed, or when mixed with glycerin or any other substance which raises the specific gravity. It is claimed that such emulsions remain stable even at a temperature of 100° C. (With regard to the process of manufacturing these amides see below, "Fatty Acid Industry.") The presence of fatty amides may be shown by treating the substance with caustic alkali and distilling off the ammonia formed, as in *Kjeldahl's* method. If stearo-anilide is present the alkaline solution must be distilled in a current of steam.

Besides those mentioned above, a number of other emulsifiers [3] have been proposed, notably those mentioned already under "Margarine," viz. yolk of egg,[4] lecithin,[5] and cholesterol. The alkali salts of naphthenic acids or of sulphonated naphthenic acids has also been proposed.[6]

The great emulsifying power imparted to mixtures of oils and fats by the addition of wool grease or wool fat will be more appropriately considered in the section "Technology of Waxes"; preparations containing wool fat have been mentioned already incidentally under "Greases" and "Emulsion Wool Oils." Very likely it is due to the fact that wool fat possesses considerable emulsifying powers that some inventors claim cholesterol and even ceryl alcohol, typical constituents of wool fat, as emulsifying agents.[7]

The manufacture of emulsion requires only simple machinery. In fact, any vessel provided with agitators geared up to a high speed will be found satisfactory (cp. "Margarine" and "Manufacture of Lubricating Greases"). *Pirsch* [8] suggests for this purpose the employment of injectors; the Swedish "Aktiebolaget Separator" has patented a number of centrifugal emulsors.[9] There appears, however, to be no need for elaborate apparatus of this kind. For laboratory apparatus designed to test the susceptibility of mineral oils to form emulsions, the papers given in the footnote should be consulted.[1]

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[1] French patent 343,158.

[2] German patent 188,712. The corresponding English patent is taken in the name of O. A. H. H. Kösters (English patent 4688, 1906).

[3] Cp. *e.g.* J. P. van der Ploeg, English patent 7699, 1908; German patent 191,399 (pyridine, quinoline); also saponin (see Vol. I. Chap. II.) and albumen solutions have been recommended.

[4] Wörner, German patent 175,381; English patent 1719, 1906.

[5] Sarason, *Pharm. Zeit.*, 1904 (92), 978; German patent 172,758; J. H. Long and F. Gephart, *Journ. Amer. Chem. Soc.*, 1908, 895. Ulzer and Batik (German patent 193,189) claim as an emulsifier a product prepared from diglycerides and phosphoric acid, in short, an artificially prepared lecithin. Cp. footnote 5, p. 143, and Vol. I. Chap. I.

[6] For their detection, see J. Marcusson, *Mitt. k. Materialprüf.*, 1918, 36, 107.

[7] Arellendorff and Kopp, *Rev. des prod. chim.*, 1904.

[8] French patent 375,594; English patent 17,976, 1907.

[9] Cp. German patents 204,061, 204,062 (W. G. Schroeder) and p. 34.

Frequently the problem arises to "break" ("de-emulsify") emulsions which have been obtained unwittingly, as in the process of refining rancid oils and fats, where the soap formed in neutralising free fatty acids leads to persistent emulsions. Intimate emulsions are also frequently formed in residues ("foots") from expressed oils, especially in the case of oils obtained from fruits, such as olive oil. Thus the finally expressed olive pulp (*crasses d'huile d'olive*) consists of an intimate mixture of pulp and water, which holds the remainder of the olive oil in so intimate an emulsion that it cannot be recovered by expression; if recourse cannot be had to the extracting of the residue with a volatile solvent, preceded by drying to remove the water, treatment with strong sulphuric acid is resorted to[2] (although this necessarily leads to the destruction of some of the fatty material). The same agent is used in breaking the emulsion obtained in the "fermentative process" of preparing "Fatty Acid Soap Stock" (see below). The problem of separating emulsions attains great importance in the case of condensed water from steam engines, where a small amount of oil in an extremely finely divided condition has to be removed from a large bulk of water. This has been done by *Hatschek*[3] by filtering the oil-containing water over calcium carbonate, which has the property of retaining small quantities of oil. The separation of oil from condensed water has also been done by passing an electric current through the water using an anode of ferrous carbonate.[4] For the action of centrifugal machines see a paper by *E. Ayres*.[5]

No general rule can be laid down as to what means must be used to "break" emulsions,[6] but, in general, it will be found that either heat assisted by agitation, or addition of acids, or of easily soluble salts,[7] will produce the breaking up of an emulsion. In emulsions where the colloid is white of egg or albuminoids of a similar nature, separation may be obtained by the addition of formaldehyde.[8] According to *Fanto and Stritar*,[9] separation can be effected by passing an electric current through the emulsion. Cp. also *Frye*, Vol. II. p. 788. *Fresenius*[10] tries to break the emulsion of coconut oil and dilute soap solution by applying an inert gas under pressure. (Cp. also Vol. I. Chap. VI. under "Unsaponifiable Matter.")

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[1] Phillips, *Journ. Soc. Chem. Ind.*, 1915; Herschel, Bureau of Standards, Washington D.C.; Bryan, Experimental Station, Navy Department, Annapolis, Ind.; P. H. Conradson, *Journ. Ind. and Eng. Chem.*, 1917, 166; W. H. Herschel, *Journ. Soc. Chem. Ind.*, 1917, 497.

[2] Cp. also R. Bernard, French patent 325,966.

[3] English patent 26,228, 1908.

[4] Goodwin and Ellis, *Chem. Zeit.*, 1910, 724; cp. also Hatschek, *Journ. Soc. Chem. Ind.*, 1910, 125.

[5] *Journ. Soc. Chem. Ind.*, 1916, 676.

[6] Cp. Bontoux, *Les Matières grasses*, 1911, 2119.

[7] Cp. G. Bottaro, French patent 476,492, 1914, and United States patent 1,159,355, 1915. Also S. S. Bhatnagar, *Chem. Soc. Trans.*, 1921, 119, 61.

[8] Rost, French patent 440,474; German patent 251,848.

[9] *Journ. prakt. Chem.*, 1910, 564.

[10] German patent 171,668.

In analytical operations emulsions are broken by judicious admixture of alcohol, ether, caustic soda solution, or salt solutions. For the filtration of colloidal solutions *Schoep*[1] claims that the addition of glycerin to the ether alcohol solution of nitro cellulose produces a membrane which permits of much greater rapidity of filtration.

A curious patent claiming the treatment of oils and fats, with oxygen, ozone, or nitric acid, so as to render them practically non-emulsifiable, has been taken out by *M. Bergés*.[2]

B.—INDUSTRIES IN WHICH THE GLYCERIDES UNDERGO A CHEMICAL CHANGE, BUT ARE NOT SAPONIFIED

These industries involve operations in which the glycerides undergo a more or less pronounced chemical change without, however, being broken up into their constituents—fatty acids and glycerol. The subject matter will be considered under the following heads :—

I. Hydrogenated oils and fats.
II. Iodised, brominated, chlorinated, sulphurised oils and fats.
III. Polymerised oils.
IV. Boiled oils.
V. Oxidised oils, Ozonised oils.
VI. Vulcanised oils.
VII. Nitrated oils.
VIII. Sulphonated oils, Turkey-red oils.

I.—HYDROGENATED FATS, HARDENED FATS

The production of solid fats from liquid oils by the direct addition of hydrogen to the glycerides of the unsaturated fatty acids has grown enormously of late years, and a very large amount of oil is so hardened annually.

Prior to the publication by *Sabatier and Senderens* in 1900 of their researches on the action of metallic catalysts, attention had been directed principally to the hydrogenation of the fatty acids as oleic acid (see under " Conversion of Oleic Acid into Candle Material "), few attempts being made to hydrogenate the glycerides. Since, however, it has been shown that unsaturated fatty acids in the combined state will take up hydrogen in the presence of metallic catalysts, a great impetus has been given to this branch of technical chemistry, and a large number of processes and catalysts have been devised for this purpose. Among the earliest patents taken out in this country is that of *Normann*.[3] *Sabatier and Senderens*[4] state that the vapour alone of the unsaturated body to be hydrogenated must come into contact with the catalytic material. Following on this observation, *Bedford*[1] sprayed the oleic acid mixed with hydrogen on to a portion of the catalyst which he kept at a temperature of about 200° C. The mixed vapours of partially reduced oleic acid and hydrogen were then passed over a fresh portion of catalyst under diminished pressure and finally through a condenser. Another process in which the oleic acid is vaporised is that due to *Schwoerer*.[2] Processes in which the unsaturated fatty acids are first converted into vapour are attended by the disadvantage that hydrocarbons may be formed by the degradation of the fatty acids, and also polymerisation products may result. These processes cannot, therefore, be applied to the hydrogenation of the glycerides which cannot be distilled without undergoing decomposition.

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[1] *Bull. Soc. Chim. Belg.*, 1910, xxiv. 354.

[2] French patent 378,706.

[3] English patent 1515, 1903.

[4] *Ann. de chem. phys.*, 1905, 335.

For the successful carrying out of the operation it is essential that the oil surrounding the catalyst be continually replaced, and also that a large surface of oil is exposed to the hydrogen. The rate of stirring and the pressure employed have a direct bearing on the speed with which hydrogen is assimilated.[3]

Various types of machines have been used to ensure a thorough intermixture of gas, oil, and catalyst.[4] In order that the reduction may take place in the shortest possible time—a point of great importance in the preparation of edible fats, continued exposure of which to a high temperature tends to impair the taste—increased pressure is employed. *Bergius*[5] states that the reaction can take place without the addition of a catalyst if the temperature and particularly the pressure are high enough. It is possible, however, that in his experiments the material of which the autoclave was made acted as an accelerator.

Mechanical stirrers presented the grave disadvantage that leakage may occur round the gland and stuffing box, causing not only loss of hydrogen but danger of explosion; hydrogen at high temperatures being such an exceedingly mobile fluid that it is extremely difficult to pack a gland so that it will not permit the passage of the gas. *Calvert*[6] has overcome this difficulty by enclosing the motor driving the stirring gear in a water-cooled chamber situated above the surface of the oil and exposed to the gas, so that no moving parts pass through the shell of the apparatus. *Lane* [1] passes the shaft carrying the stirrers through the bottom of the autoclave where there is no possibility of a leakage of gas, the join being hydraulically packed and water-cooled. *T. B. Walker* [2] sprays the oil and hydrogen against the catalytic material, passing at the same time an electrical discharge through the mass.

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[1] English patent 9112, 1908.

[2] German patent 119,909.

[3] L. Ubbelhode and T. Svanoe, *Journ. Soc. Chem. Ind.*, 1919, 870 A. Cp. also E. B. Maxted, *Journ. Soc. Chem. Ind.*, 1921, 169 T.

[4] Kayser, United States patent 1,004,435; Testrup, English patent 7726, 1910; Wilbuschewitsch, French patent 426,343; United States patent 1,079,278; Ellis, United States patents 1,026,156, 1,040,531, 1,040,532, 1,084,202; Humphreys, United States patent 1,100,735; David, French patent 470,392; Hart, English patent 27,654, 1912; J. Dewar and A. Liebmann, English patent 15,668, 1914, United States patent 1,275,405, 1918; K. M'Ilroy, United States patent 1,157,993, 1915; A. Woltman, English patent, 112,293, 1916; A. H. Ney, United States patent, 1,185,704, 1916; H. Moore, United States patent, 1,184,480, 1916; E. Maxted and G. Risdale, English patent 13,837, 1916; M. Ittner, United States patents 1,271,575 and 1,271,576, 1918; K. Birkeland and O. Devik, United States patent 1,125,259, 1915; A. H. Charlton, English patent 1410, 1914; G. Martin, English patent 129,461, 1918; D. Blair and J. Ferguson, English patents 144,478 and 144,479, 1919.

[5] *Zeits. f. angew. Chem.*, 1914, 522.

[6] French patent 468,426; English patent 18,350, 1913; G. Calvert, English patent 5967, 1914, and United States patent 1,142,668, 1915.

Paal and Roth hydrogenate in the cold by the use of colloidal palladium.[3] Platinum has also been proposed,[4] but this is more sensitive to poisonous influences than is palladium [5] (cp. Vol. I. p. 61). An enormous number of patents have been taken out relating to the preparation of catalysts, of which space forbids more than a selection. Among the metals claimed are iron,[6] copper, vanadium,[7] osmium,[8] ruthenium,[9] and beryllium. The catalyst which finds most employment on a commercial scale is, however, nickel, combining, as it does, low initial cost with great efficiency. It is used either as a finely divided metallic powder (the use of nickel in the form of extremely thin sheets has been patented [10]), oxide,[11] suboxide,[12] borate,[13] carbide,[14] or in order to increase the contact surface it is deposited on an inert substance like carbon,[15] kieselguhr,[16] silica [17] or alumina silicate.[18] Other salts of organic acids which have been proposed are the formates,[19] acetates,[20] lactates, oleates,[21] benzoates,[22] and glycerates [23] of copper, iron, nickel, and cobalt.[24] Nickel has also been used in the form of basic salts with fatty acids of high molecular weight.[25] *Shukoff* [26] passes hydrogen containing a small proportion of nickel carbonyl through the oil heated to a temperature sufficiently high to decompose the nickel carbonyl; leaving the metallic nickel in a very finely divided form disseminated through the oil, although carbon monoxide is stated by *Maxted*[1] to exercise a poisonous influence on the catalyst. *Dewar and Liebmann*[2] prepare a catalyst from a mixture containing the oxides, hydroxides, or carbonates of two or more of the metals nickel, cobalt, copper, or iron with or without the addition of silver oxide, which is then reduced at a low temperature. *Fox*[3] heats nickel carbonate immersed in oil to 230° C. in an atmosphere of hydrogen, until the nickel has been reduced, after which the temperature may be allowed to fall. Fluorine, tellurium, or antimony in combination with a catalytic metal such as nickel are stated to form a very active catalyst with which fats may be hydrogenated at 100° C.[4] *W. Richardson*[5] patents an electrolytic method of preparing nickel powder, and also a mechanical method in which nickel shot is abraded in a ball mill.[6]

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[1] English patent 968, 1915, and 21,895, 1918.

[2] United States patent 1,123,962, 1915. Cp. also W. Richardson, United States patent 1,177,896, 1916.

[3] Cp. also G. Verona, *Rinati Annali Chim. Appl.*, 1914, **2**, 99; N. Sulzberger, United States patent 1,171,902, 1916; F. Nord, *Zeits. f. angew. Chem.*, 1919, **32**, 305.

[4] Cp. Skita, *Zeits. f. angew. Chem.*, 1913, 601; *Chem. Zeit.*, 1914, 605; English patent 16,283, 1913.

[5] Wieland, *Berichte*, 1912, 2615.

[6] A. G. Müller, German patent application, M. 47,644.

[7] *Soc. Anon. Conidelon*, English patent 5174, 1913.

[8] Normann and Schick, *Archiv d. Pharm.*, 1914, (252), 208.

[9] *Badische Anilin u. Soda Fabrik.*

[10] Hagemann and Baskerville, United States patent 1,083,930.

[11] Erdmann, *Zeits. f. angew. Chem.*, 1913, 606.

[12] Bedford and Williams, French patent 436,295.

[13] French patent 470,364, 1914. Cp. also H. Schonfield, *Zeits. f. angew. Chem.*, 1916, **29**, 39. Cp. also E. Erdmann and E. Rock, *Zeits. f. angew. Chem.*, 1915, **28**, 220; W. Normann, *Zeits. f. angew. Chem.*, 1915, **28**, 220.

[14] C. Ellis, United States patents 1,182,995, 1,184,086, and 1,185,075, 1916.

[15] Ellis, United States patent 1,084,258.

[16] Bremen, *Besigheimer Ölfabrik*, German patent application W. 37,440.

[17] N. Sulzberger, United States patent 1,143,332. Cp. E. Sittig and A. Granichstädten, English patent 147,578, 1920, also C. Bosch, C. Schmidt, and A. Mittasch, United States patent 1,391,666, 1921.

[18] J. Y. Johnson, English patent 8462, 1914. Cp. also G. Grote, *Seifensieder-Zeit.*, 1920, 713.

[19] W. Snelling, United States patent 1,112,811, 1914. Cp. also E. Higgins, English patent 23,873, 1913; C. Ellis, United States patent 1,296,496, 1917.

[20] C. Ellis, United States patent 1,251,203, 1917.

[21] W. Richardson, United States patent 1,151,718, 1915; C. Ellis, United States patent 1,251,201, 1917.

[22] Bremen, *Besigheimer Ölfabriken*, English patent 4023, 1915.

[23] B. Van Eldik Thieme and A. Geitel, German patent 292,894.

[24] Wimmer and Higgins, English patent 25,326, 1911.

[25] *De Nordiske Fabriker*, French patent 462,905. Cp. also C. Ellis, United States patent 1,378,336-8, 1921.

[26] German patent 241,823. Cp. also Lessing, English patent 18,998, 1912, and C. Ellis, United States patent 1,154,495, 1915, and United States patent, 1,251,202, 1917.

The nickel catalyst is prepared either by calcining nickel nitrate (*K. Kamura*[7] roasts a salt of nickel in a current of ammonia or the vapour of an ammonium salt), or by precipitating the soluble salts of nickel with sodium hydroxide, carbonate, or ammonia,[8] after which the insoluble nickel salts are washed and ignited at a low temperature, and reduced by passing hydrogen over them until water is no longer evolved. An apparatus for effecting the reduction of the nickel oxide has been patented by *H. Lane*.[9] The temperature at which reduction is carried out varies with the method of preparation of the oxide or hydroxide.[10] As a rule, the lower the temperature at which the reduction of the catalyst is carried out, the higher will be its activity. *Senderens and Aboulenc*[11] point out that reduction of the oxide prepared by the spontaneous oxidation of the previously reduced metal, or by gently heating the reduced metal, can be effected at a lower temperature than the oxide prepared by calcining nickel nitrate, and gives a catalyst of a higher degree of efficiency. They also state that the exhausted catalyst may be regenerated by passing oxygen over it and finally reducing it with hydrogen. For recovering the catalyst, a patent has been taken out according to which the spent material is first ignited to drive off the organic matter, and the nickel oxide dissolved in mineral acids and reprecipitated.[1] *Wilbuschewitsch* [2] extracts the catalyst with a solvent, dissolves the metal in acid, and precipitates with sodium carbonate solution.

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[1] *Journ. Soc. Chem. Ind.*, 1918, 9 R.; and *Faraday Soc.*, Dec. 1917.

[2] English patents 12,981 and 12,982, 1913.

[3] English patent 11,542, 1913. Cp. also A. Brochet, *Bull. Soc. Chim.*, 1920, **27**, 899 and Soc. de Stéarinerie et Savonnerie de Lyon, and P. Berthon, English patent 107,004, 1917.

[4] German patent 282,782 (Badische Anilin and Sodafabrik Co.).

[5] United States patent 1,175,905, 1916; United States patents 1,257,396, 1,257,397, and 1,257,531, 1918.

[6] *Chem. and Met. Eng.*, 1920, **22**, 793.

[7] English patent 12,032, 1917.

[8] D. Wesson, United States patent 1,143,339, 1915; J. Woodruff, United States patent 1,143,343, 1915.

[9] English patent 115,924, 1917.

[10] *Bull. Soc. Chim. de France*, 1912, 642. Cp. also C. Kelber, *Berichte*, 1921, **54**, 1701.

[11] *Bull. Soc. Chim. de France*, 1912, 643.

The higher the activity of the catalyst, the greater will be its sensibility to poisonous influences, such as chlorine, arsenic, sulphur, and phosphorus. According to *Paal and Karl*,[3] basic lead carbonate destroys the activity of a palladium catalyst completely. Zinc oxide, aluminium hydroxide,[4] and ferric hydroxide greatly reduce it, whereas magnesium and magnesium oxide were without influence. Similar results have been found by *Paal and Windisch* [5] for the platinum catalyst. *Fuchs* [6] heats the hydrogen to 200-250° C. before passing into the oil, and states that its activity is increased by exposing it to the chemically active light rays. The activity of a nickel catalyst is adversely affected by the presence of soaps of the alkali metals, barium, chromium, iron, zinc, cadmium, lead, mercury, bismuth, and tin. Proteins also showed an inhibitive effect.[7] The separation of the spent catalyst from the oil after the process of reduction had been completed presented great mechanical difficulties, the nickel being in such a finely divided condition that ordinary filter cloth was too coarse in mesh to prevent the passage of some particles. In some cases the nickel was successfully removed by using two thicknesses of a close-textured filter-cloth with a sheet of filter paper between them. Another device is to add fuller's earth [8] or china clay to the oil before filtering. A magnetic method of separation has been patented.[9]

Whether the reduction is effected by metallic metal or by the oxide or suboxide of nickel must in the present state of our knowledge be regarded as an open question. *Normann* [10] is of the opinion that nickel in the metallic state is the active agent, and his view has been hotly contested by *Erdmann and Bedford* [11] without, however, any decisive result being attained.

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[1] A. Jürgens, German patent application, N. 13,908; H. Morrison, United States patent 1,203,233, 1916; H. Schlinck and Co., German patent 313,192; S. and G. Müller, German patent 319,332, 1918.

[2] French patent 426,343. Cp. also Soc. Ind. de Prod. Chimiques, English patent 112,768, 1917.

[3] *Berichte*, 1913, 3069. Cp. also E. Maxted, *Chem. Soc. Trans.*, 1920, **117**, 1501, 1921, **119**, 1280; and C. Paal and G. W. Hartmann, *Berichte*, 1918, **51**, 711, 894; also E. B. Maxted, *Chem. Soc. Trans.*, 1921, **119**, 225.

[4] In spite of this, aluminium hydroxide has been proposed as a carrier for nickel, United States patent 1,152,591, also A. Spieler, United States patent 1,139,592, 1915. Cp. also L. Kahlenberg and G. J. Ritter, *Journ. Phys. Chem.*, 1921, **25**, 89.

[5] *Berichte*, 1913, 4010.

[6] French patent 458,445.

[7] S. Ueno, *Journ. Chem. Ind. Tokyo*, 1918, **21**, 898. Cp. also W. Bancroft, *Amer. Elec. Soc.*, 1917.

[8] M. Whitaker, United States patent 1,242,624, 1917; C. Ellis, United States patent 1,224,291, 1917.

[9] Soc. L'Oxylithe and J. Walter, French patent 471,108, 1914.

[10] W. Normann and W. Pungs, *Chem. Zeit.*, 1915, **39**, 29, and 41; W. Normann, *ibid.*, 1916, **40**, 381. Cp. also W. Meigen, *Journ. prakt. Chem.*, 1915, **92**, 390.

[11] *Journ. Soc. Chem. Ind.*, 1913, 611; E. Erdmann, *Journ. prakt. Chem.*, 1915, **91**, 469. Cp. also J. B. Senderens and J. Aboulenc, *Bull. Soc. Chim.*, 1915, **17**, 14; W. Siegmund and W. Suida, *Journ. prakt. Chem.*, 1915, **91**, 442. and J. Boeseken, *Rec. Trad. Chim. Pays-Bas*, 1914, **15**, 783.

For the theory underlying contact action the work of *E. F. Armstrong and T. P. Hilditch* [1] should be consulted.

Most oils in their crude state contain substances which poison the catalyst, causing not only a retardation of the process, but also a large expenditure of the catalyst. These substances are most likely of an albuminoid nature, and must be removed by careful refining before the oil is hydrogenated. "Oxidised acids," particularly in the case of fish oils, exercise a pronounced poisoning effect. In most cases the removal of the free fatty acids coupled with a simple treatment is sufficient to remove the poisonous substances. The refining of fish oils, however, presents a very difficult problem, as they require a special method of treatment. The method proposed by *Ellis and Wells*,[2] which consists in agitating the oil with spent catalyst or with copper or nickel hydroxide, is expensive and does not answer with rank dark oils. Instead of removing the free fatty acids *C. Dreymann* [3] converts them into their ethylic esters.

Hydrogenated fats, particularly those prepared from vegetable oils, are finding increasing use in the edible fat industry to replace the more expensive animal fats in the manufacture of margarine and of lard substitutes. Suitably hardened, they should also find an outlet in the manufacture of chocolate fats. If the hydrogenation is carried out to too great an extent, the fat, owing to its high melting point, would probably be indigestible if used alone (cp. p. 25), and would therefore have to be brought to a softer consistence by admixture with a liquid oil. Since the hydrogenation is also accompanied by the deodorisation of the oil, and since, if the operation is carefully conducted, a diminution of the taste ensues, it will be preferable to harden the oil only to the desired consistence instead of hardening a portion completely to stiffen the bulk of the oil. The use of hardened fish, liver, and blubber oils in the edible fat industry was looked upon with disfavour before the war by medical opinion in Germany and Austria, although if the oil be prepared from fresh fish or blubber oils and well refined, there is no apparent reason why they should not be used if the natural prejudice of the public against oils from such sources can be overcome.

Hardened fats which are intended to be used for edible purposes should be as free as possible from traces of nickel. If the oil was neutral before hardening, and the operations have been conducted with due care, the final product should be completely free from nickel or at the most contain 0·1 milligramme per kilo. *Lehmann* [4] states that no harmful effects were observed after feeding human beings on hardened arachis, sesamé, and cotton seed oils which contained up to 6 milligrammes of nickel per kilo. That this view is correct is borne out by the work of *Erlandsen, Fridicia and Elgström*,[5] and also *Thomas and Müller*.[6]

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[1] *Journ. Soc. Chem. Ind.*, 1919, 226 R.; and *Proc. Roy. Soc.*, 1919, A, **96**, 137, 1920, A, **98**, 27. Cp. also W. Bancroft, *Amer. Elec. Soc.*, 1917, and W. C. M'C. Lewis, *Chem. Soc. Trans.*, 1920, **117**, 623.

[2] *Journ. Ind. and Eng. Chem.*, 1916, 8, 886. Cp. also United States patents 1,247,516, 1917, and 1,132,710, 1915.

[3] United States patent 1,228,888, 1917.

[4] *Chem. Zeit.*, 1914, 798.

[5] *Tidschrift Kem.*, 1918, 109.

[6] *Arch. Hyg.*, 1915, 56.

Fahrion[1] concludes that there is no hygienic reason against the use of hardened fats in general, including hardened fish oils.

Processes for preparing edible fats by hydrogenation have been patented.[2] An Austrian patent[3] has been applied for for hydrogenating fats in the presence of glycerin, whereby it is stated that the free fatty acids are converted into neutral glycerides. Hardened cotton seed oil has been used successfully to replace palm oil in the tin-plating industry.[4] The value of hardened fats in the soap and candle industries is discussed below under "Soap Manufacture" and "Candle Manufacture."

The hydrogenation of colophony has been patented.[5]

The detection of hardened oils in mixtures presents a very difficult problem. Since all the unsaturated fatty acids containing eighteen carbon atoms are reduced to stearic acid, the characteristic difference between drying oils and non-drying oils and fats is destroyed, and hence the hexabromide test is rendered nugatory. Erucic acid present in rape oil and fish oils is reduced to behenic acid, which may be isolated by the method described in Vol. I. p. 564. Thus in a hardened whale oil of the iodine value 59·8 *B. Svendsen*[6] found 2·5 per cent of behenic acid.

The chromogenetic substance giving rise to the colour reactions in cotton seed oil is destroyed or, at least, changed; thus the author found the *Halphen* reactions of a sample of hardened cotton seed oil which had the iodine value of 104 to be very faint, whilst when the hydrogenation had been carried farther, until the iodine value was 98, the oil no longer gave the reaction.[7] The *Baudouin* test gives very erratic results. In the samples examined by *Bömer*[8] and also by *Kreis and Roth*[9] it was shown that this colour test is intensified, although in two samples examined by the author no coloration was obtained. The substances yielding the characteristic blue coloration of liver oils with sulphuric acid are destroyed (cp. Vol. I. p. 509).

M. Tortelli and E. Jaffe[10] propose a new colour test for hardened marine animal oils. The test is carried out as follows: 1 c.c. of the melted fat is placed in a stoppered cylinder and dissolved in 6 c.c. of chloroform and 1 c.c. of glacial acetic acid. To this are added forty drops of a 10 per cent chloroformic solution of bromine, and the cylinder shaken vigorously. The presence of marine animal oils is shown by the appearance of a fugitive rose coloration changing to bright green. This test has been condemned by *J. Davidsohn*[1] on the ground that hydrogenated vegetable oils also give a green coloration. This observation can be confirmed in some instances by the present writer.

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[1] *Chem. Umschau*, 1919, **26**, 22 and 33. Cp. also Bordas, *Ann. des falsif.* 1919, **12**, 225. Cp. A. D. Holmes and H. J. Deuel, *Amer. Physiol.*, 1921, **54**, 479; also E. Rost, *Arbb. Reichs-Gesundh.-Amt*, 1920, **52**, 184.

[2] Ellis, United States patents 1,058,738, 1,087,161, 1,095,144; French patent 461,647; English patent 18,376, 1913; Déveaux, French patent 458,611; Lessing, English patent 18,998, 1912; Maxted and Risdale, English patent 109,993, 1917.

[3] *Ölverwertung G. m. b. H.*, Austrian patent application, A. 7293. Cp. also C. Ellis, United States patent 1,261,911, 1918.

[4] *Journ. Ind. and Eng. Chem.*, 1920, 149.

[5] B. Brooks, United States patent 1,167,264, 1916.

[6] *Zeits. f. angew. Chem.*, 1917, **30**, 95.

[7] Cp. also H. K. Moore, G. Richter, and W. Van Ardsel, *Journ. Ind. and Eng. Chem.*, 1917, 451.

[8] *Chem. Revue*, 1912, 218 and 247.

[9] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1913, xxv. 81.

[10] *Annali Chim. Applic.*, 1914, **2**, 80.

In the case of castor oil the acetyl value may be lowered, the extent of the decrease depending on the temperature to which it has been subjected in the reduction. Thus in two samples examined by *Normann and Hugel*[2] the acetyl value had fallen from 156 to 102 and to 131 (cp. Vol. I. p. 219).

If the hydroxyl group has not been split off, the hardened castor oil is soluble in alcohol, and behaves with petroleum ether in a similar manner to unchanged castor oil, while if the hydroxyl group has been removed, the resulting fat is insoluble in alcohol and simulates in its behaviour fats rich in stearin. *Grün*[3] differentiates hardened marine animal oils from hardened rape oil by isolating and identifying the palmitic acid contained in the former. For his somewhat cumbersone method, which involves the fractionation of the methylesters, the original paper should be consulted. Hardened vegetable and animal fats may be differentiated by means of the phytosterol acetate test. If the temperature of reduction has been allowed to rise to too high a degree, hydrocarbons may be formed, and also the cholesterol may have become resinified, vitiating its separation by means of digitonin. Phytosterol is said to be unaffected.[4] The melting points and crystalline forms of the sterols, and also of their acetates isolated from vegetable and animal fats, are stated by *Bomer*[5] to be unaffected by the hardening process. This observer also states that the difference value by *Polenske's* method (cp. Vol. I. p. 331) of hardened arachis and sesamé oils is lower than that of lard, whereas in the case of whale oil the difference value approximates that of tallow. The following table due to *Bömer*[6] illustrates this point:—

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[1] *Zeits. f. angew. Chem.*, 1915, **28**, 560. Cp., however, J. Prescher, *ibid.*, 1916, **29**, 165.

[2] *Chem. Zeit.*, 1913, 815. Cp. also T. Jurgens and W. Meigen, *Chem. Umschau*, 1916, **23**, 99, 116.

[3] *Chem. Umschau*, 1919, **26**, 101.

[4] Marcusson and Meyerheim, *Zeits. f. angew. Chem.*, 1914, 201.

[5] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912, xxiv. 108.

[6] *Ibid.*, 1912, xxiv. 107.

Hardened Fat.	Melting Point.	Solidifying Point.	Difference Value.	Refractometer Value at 40°.	Acid Value.	Saponification Value.	Iodine Value.
Arachis oil . . .	...	...	...	56·8	1·1	191·1	84·4
,, . . .	51·2	36·5	14·7	50·1	1·0	188·7	47·4
,, . . .	44·2	30·2	14·0	52·3	1·3	188·3	56·5
,, . . .	46·1	32·1	14·0	50·5	0·9	188·4	54·1
,, . . .	53·5	38·8	14·7	49·0	1·2	189·0	42·2
,, . . .	43·7	27·7	14·0	51·7	2·3	191·6	61·1
Sesamé oil . . .	47·8	33·4	14·4	51·5	0·5	190·6	54·8
,, . .	62·1	45·3	16·8	38·4 (at 50°)	4·7	188·9	25·4
Cotton seed oil . .	38·5	25·4	13·1	53·8	0·6	195·7	69·7
Coconut oil . . .	25·6	20·4	5·2	37·4	0·3	255·6	11·8
,, . . .	44·5	27·7	16·8	35·9	0·4	254·1	1·0
Whale oil	45·1	33·9	11·2	49·1	1·2	192·3	45·2
,, ...	45·4	33·7	11·7	49·1	1·1	193·0	46·8

The following table contains some characteristics of hardened fats. Further details will be found under the heading of each individual fat in Vol. II. :—

Hardened Fat.	Oil.					Fatty Acids.			
	Melting Point ° C.	Saponification Value.	Iodine Value.	Solidifying Point.	Butyro Refractometer 60° C.	Solidifying Point.	Melting Point.	Mean Molecular Weight.	Melting Point of Arachidic Acid.
Cotton seed [1]	59	192·3	41	...	...	50·3	57	...	...
Kapok seed [1]	55	191	32	...	39	48	53	...	...
Soya bean [1]	68	190·9	15·2	...	42	61·2	66	...	...
Whale oil [1]	52·2	169·5	28·8	...	29·5	44	49	...	...
" [2]	48-50	191·6	24·5	...	...	...	48	...	...
Cod liver oil [3]	41·9	190·9	57·8	31·9	48·2 (40° C.)	...	...	282·0	76·0
Sperm oil [3]	50	131·7	17·3	...	...	39	48	...	...

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[1] Mellana, *Ann. Chim. Appl.*, 1914, i. 381.

[2] Unpublished observation. The sample contained 0·33 per cent free fatty acids and 2·91 per cent of unsaponifiable matter.

[3] Sandelin. *Teknikern*, 1913, 359.

The following table due to *C. Mannich and E. Thiele*[1] contains some characteristics of completely hydrogenated fats :—

Hydrogenated Oil.	Melting Point.	Iodine Value.	Saponification Value.	Melting Point of Insoluble Fatty Acids.
	°C.			°C.
Olive	70	0·2	190·9	71
Almond . . .	72	0·0	191·8	71
Arachis . . .	64-64·5	0·0	191·6	67
Sesamé . . .	68·5	0·7	190·6	69·5
Cacao butter. .	63·5-64	0·0	193·9	65·5
Poppy seed . .	70·5	0·3	191·3	71
Linseed . . .	68	0·2	189·6	70·5
Tallow . . .	62	0·1	197·7	64
Lard	64	1·0	196·8	62
Cod liver . .	65	1·2	186·2	59

II.—IODISED, BROMINATED, SULPHURISED OILS AND FATS

The oils belonging to this group have been introduced into pharmaceutical practice.

The assumption that the therapeutical effect of cod liver oil is due to the small amount of iodine it contains led to the manufacture of *iodised* or *brominated* oils and fats. They are prepared by allowing oils and fats to absorb a certain amount of iodine[2] or bromine. The method of preparing these oils and fats was at first carried out on the lines suggested by the analytical operations involved in the methods of determining the iodine and bromine values (described, Vol. I. Chap. VI.), *e.g.* by treating with iodo-chloride or bromine.[3] Later on gaseous hydriodic and hydrobromic acids[4] were substituted for the halogens themselves; or hydriodic and hydrobromic acids were used in *statu nascendi* in aqueous solution.[5] The production of iodised and brominated oils by treating with halogen in the presence of the sulphydrate of a chlorinated aldehyde, *e.g.* chloral sulphydrate, has been patented.[6]

The oils and fats selected for these preparations are sesamé oil, almond oil, and lard. The commercial preparations "Iodipin" and "Bromipin" are respectively the iodine and bromine compounds of sesamé oil. Similar products have been prepared from coconut oil and cacao butter.[7] Bromipin is prepared in two strengths, viz. bromipin containing 10 per cent of bromine, and bromipin containing 33·3 per cent of bromine. Iodipin is also prepared in two strengths, containing respectively 10 per cent and 25 per cent of iodine. As sesamé oil absorbs about 106-110 per cent of iodine, it is evident that the saturation of the doubly-linked carbon atoms has only taken place in a portion of the oil. For the glycerides of the fatty acids the methyl- and ethyl-esters of these acids have also been substituted.

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[1] *Ber. Deutschen Pharm. Ges.*, 1916, 26, 36.

[2] Iodised oils, R. R. Seifert and E. Merck, United States patent 913,311.

[3] German patent 96,495; E. Merck, *Zeits. f. angew. Chem.*, 1898, 398.

[4] English patent 11,494, 1902; German patent 135,835; French patent 230,993 (W. Majert).

[5] German patent 159,748 (Merck).

[6] Voswinkel, German patent 233,857.

[7] H. A. Pryor (*Chem. Fab. von Heyden*), English patent 3132, 1906.

The taste of these compounds appears to have been found objectionable; hence a patent has been taken out for the conversion of the iodised and brominated oils into a powder by mixing them with casein and milk sugar.[1]

By the action of chlorine on cod liver oil at 90° C., *L. Meunier and L. Wierzchowski*[2] prepared a chlorinated cod liver oil with a specific gravity of 0·9950 and containing 6·95 per cent of oxidised fatty acids and 12·80 per cent of chlorine. A similar preparation from linseed oil had the specific gravity 1·0137 and contained 12·23 per cent of chlorine. In both cases the viscosity had increased and the products are stated to have emulsifying properties.

Chlorinated oils have been claimed (in conjunction with albuminate of calcium) for the production of paints.[3]

Latterly, even *sulphurised* compounds are being manufactured on the lines of the sulphur chloride method described in Vol. I. Chap. VII. Sulphurised fats are also prepared by saponifying oils or fats in the usual manner, liberating the fatty acids, and converting these into their ethylic and methylic esters.[4] The latter are then dissolved in carbon tetrachloride, and sulphur chloride is added (cp. also "Vulcanised Oils," below). The product is washed with water and sodium carbonate solution, then again with water, after which the carbon tetrachloride is distilled off, and the residue washed again thoroughly with dilute caustic soda or a solution of sodium sulphide, and finally with water. A product thus prepared on a commercial scale contained 6·4 per cent of sulphur.

By the combined action of halogens and of sulphur compounds on sesamé oil, a preparation containing both iodised and sulphurised compounds is produced.[5] According to the patent specification, sesamé oil or poppy seed oil is first treated with a solution of iodine in benzene; into this solution sulphuretted hydrogen gas is passed. Thus products containing from 10 to 30 per cent of iodine and about 2 per cent of sulphur are obtained.

Similar preparations obtained from fatty acids will be described in the next section of this chapter under "Fatty Acid Manufacture."

Mercurised oils and fats are prepared by dissolving mercuric chloride or mercuric iodide in anhydrous acetone or ether, shaking the solution with the oil, and subsequently distilling off the solvent,[6] or by heating the oil with mercuric chloride whereby some of the mercury is retained by the oil in a colloidal form.[7]

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[1] English patent 3430, 1903; cp. also German patent 200,291 (E. Merck).

[2] *Zeits. f. angew. Chem.*, 1915, 28, 98.

[3] A. Brunstein, German patent 186,272; Boehringer u. Söhne, German patents 248,779, 258,856, 258,156; Belgian patent 249,089; Lake, English patents 9023, 9027, 1911; Electrolytic Alkali Co., Connor and Stubbs, English patent 741, 1908.

[4] W. Majert, French patent 328,993; English patent 11,404, 1902; German patent 140,827.

[5] English patent 24,321, 1901; United States patent 696,900; cp. also Loebell, English patent 27,105, 1904; German patent 169,491.

[6] Glock, German patent 246,507.

[7] Dering, German patent 239,681; English patent 1219, 1912.

III.—POLYMERISED OILS

The author comprises under the term "polymerised oils" those products which are obtained by heating certain oils, with or without condensing agents (see below), to a somewhat elevated temperature. The chemical changes which occur are not yet fully understood; in the absence of a satisfactory explanation, they may, therefore, be conveniently summarised under the term "polymerisation." Determinations of the molecular weight of linseed oil products by the freezing point method[1] have indeed shown that they possess double the molecular weight of linseed oil (see Vol. I. Chap. XII.). That light is unnecessary to the drying of linseed oil has been shown by *P. Slansky*.[2] Typical polymerised oils are obtained from (1) linseed oil, (2) tung oil, (3) safflower oil, (4) castor oil, (5) sterculia oil. It has been shown by *A. Kronstein*[3] that all fatty oils contain some proportion of bodies which may be gelatinised by heating if the non-polymerisable portion is first removed. The amount of non-polymerisable bodies which have a retarding effect on the gelatinisation of the remainder varies for each individual oil. The amount which had to be removed from the various oils by distillation in vacuo before the remainder would set to a jelly is given in the following table. This figure is termed by *Kronstein* the "distillation number."

Oil.	Distillation Number.
Chinese Tung	0
Linseed	16·3
Perilla	18·5
Hempseed	20·5
Walnut	23·9
Poppy seed	24·7
Sunflower seed	25·0
Soya bean	25·4
Almond	33·0
Cotton seed	33·6
Maize	35·5
Rape	35·6
Sesamé	42·5
Castor	48·0
Arachis	53·0
Olive	54·0

The fatty acids obtained from polymerised linseed oil (by the usual method) also represent products of polymerisation. Polymerised oils prepared by ozonising vegetable or animal oils in the presence of mineral oils are used chiefly in the manufacture of viscous lubricating oils.[4] *Marcusson*[5] thickens oils by blowing with air followed by treatment with an electric current under reduced pressure.

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[1] Barries, *Oxydation des Leinöls, Dissert.*, Leipzig, 1902; Norman, *Chem. Zeit.*, 1907, 188; Held, *Inaug. Dissert.*, 1909.

[2] *Zeit. angew. Chem.*, 1921, 34, 68.

[3] *Berichte*, 1916, 49, 722.

[4] A. de Hemptinne, French patent 404,843.

[5] *Zeits. f. angew. Chem.*, 1920, 33, 231.

The behaviour of these oils at elevated temperatures, as also the products obtained from them, vary so considerably that each oil must be considered separately.

(1) POLYMERISED LINSEED OIL

Lithographic Varnishes

French—*Vernis d'imprimerie.* German—*Lithographenfirnis.*
Italian—*Olio da litografia.*

The commercial lithographic varnishes are prepared by heating linseed oil to 250° or to 300° C. without the addition of any drier. According to the length of time of heating the specific gravity " thickness " of the " varnish " varies. Hence the commercial lithographic varnishes are known under the trade terms " thin varnish," " medium varnish," " strong varnish," " extra strong varnish," " thick varnish," etc. These oils find application in lithographic printing and in the preparation of printers' inks. Small quantities find an outlet as " bird lime." They differ from the " Boiled Oils " (see below) by not containing any metal. By this heating process traces of moisture are driven off, the " mucilage " is coagulated, and readily separates on standing. Hence the German name for these oils is " Standöle." *Schmidt* heats the oil out of contact with air by placing a perforated plate above the surface of the oil in the heating vessel which is covered by an absorbent material such as felt, whereby the volatile products are retained.[1] In order to avoid exposure to the air and loss by volatilisation *Genthe* [2] covers the *oil* with a floating perforated cover which allows volatile gases to escape. *Genthe* recommends vessels of aluminium, as this metal is but little attacked and even then forms colourless salts.

Winkler [3] polymerises drying oils and castor oils by heating the oil with amorphous phosphorus and phenol.

" *Burnt varnish* " is a fairly quick drying oil, which will form a strong skin in twenty-four to forty-eight hours at the ordinary temperature. It is obtained by heating raw linseed oil up to its flash point, and allowing it then to burn quietly, with constant stirring, until the required consistence is reached.

The commercial lithographic varnishes are perfectly clear, transparent, viscid liquids. The thickest varnishes no longer leave a grease-spot on paper. The thin and medium varnishes are but slightly darker than raw linseed oil. Oils prepared by boiling over fire frequently exhibit a more or less strongly marked green fluorescence.

The following table contains the results of an examination by *Leeds* [4] of several lithographic varnishes, to which, for the sake of comparison, the corresponding numbers for a raw linseed oil are added :—

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[1] German patent 215,349.

[2] German patents 215,348, 222,666.

[3] German patent 252,139.

[4] *Journ. Soc. Chem. Ind.*, 1894, 203.

Lithographic Varnishes prepared by Boiling over Fire (Leeds)

	Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Oxidised Acids.	Unsaponifiable Matter.	Free Acids calculated as Oleic Acid.
		Mgrms. KOH.	Per cent.	Per cent.	Per cent.	Per cent.
Raw linseed oil . .	0·9321	194·8	169·0	0·30	...	0·85
"Tint" varnish . .	0·9584	197·5	113·2	1·50	...	1·46
"Thin" varnish . .	0·9661	196·9	100·0	2·50	0·62	1·76
"Middle" varnish .	0·9721	197·5	91·6	4·20	0·85	1·71
"Strong" varnish .	0·9741	190·9	86·7	6·50	0·79	2·16
"Extra strong" varnish	0·9780	188·9	83·5	7·50	0·91	2·51
"Burnt" thin varnish .	0·9675	195·5	92·7	0·85	1·35	6·93

The mixed fatty acids, derived from the raw linseed oil and from the "varnishes," freed from the unsaponifiable matter, gave the following results :—

Mixed Fatty Acids from Lithographic Varnishes (Leeds)

	Specific Gravity at 15·5° C.	Solidifying Point. °C.	Melting Point. °C.	Neutralisation Value. Mgrms. KOH.	Mean Combining Weight.	Iodine Value.
Raw linseed oil . .	0·923	...	24-26·5	195·8	286·5	145·5
"Tint" varnish . .	0·941	15	20·5	...	...	118·3
"Thin" varnish . .	0·949	18	22	...	...	108·8
"Middle" varnish .	0·950	22	24	205·8	272·6	97·7
"Strong" varnish .	0·953	24	25·5	207·7	270·1	87·3
"Extra strong" varnish	0·955	23	27	207·9	269·8	90·8
"Burnt" thin varnish .	...	19	23	...	...	99·3

The chemical change which the linseed oil undergoes manifests itself in an increase of specific gravity and a decrease in the iodine absorption. A slight decrease is also noticeable in the amount of free fatty acids due probably to their volatilisation,[1] although this may be in part due as suggested by *A. H. Salway* [2] to the interaction between the carboxyl group and the unsaturated radicle. *Salway* has shown that the presence of free fatty acids accelerates the reduction of the iodine value when the oil is heated in sealed tubes in an atmosphere of carbon dioxide, and notably a considerable decrease occurs in the yield of ether-insoluble hexa-bromides (*Lewkowitsch* [3]). This is illustrated by the following table, in which a typical linseed oil is contrasted with a linseed oil heated to 600° F., and with a number of commercial lithographic varnishes :—

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[1] Gardner, Carmick, and Heckel, *Drugs, Oils, and Paints*, 1913, No. 7.

[2] *Journ. Soc. Chem. Ind.*, 1920, 324 T.

[3] *Analyst*, 1904, 2.

Polymerised Linseed Oils—Lithographic Varnishes (Lewkowitsch)

	Specific Gravity at 60° F.	Saponification Value.	Iodine Value.	Yield of Ether-insoluble Bromides.	Insoluble Fatty Acids + Unsaponifiable.	Oxidised Fatty Acids.	Unsaponifiable Matter.	Glycerine obtained.	Acid Value.[1]	Acetyl Value.	Iodine Value of Fatty Acids.	Liquid Fatty Acids.[2]	Iodine Value of	
													Liquid[2] Acids.	Solid[2] Acids.
				Per cent.		Per cent.	Per cent.	Per cent.				Per cent.		
Linseed oil, raw	0·9308	...	186·4	24·17										
Linseed oil, heated to 600° F.	0·9354	...	176·3	8·44										
Thin varnish, No. I.	0·9676	189·5	107·7	0·17	94·75	4·17	1·76	9·71	6·09	6·5	114·74	39·31	131·29	106·2
,, ,, ,, II.	0·9691	193·0	125·3	2·00	94·8	0·34	0·13							
Medium ,, ,, I.	0·9693	194·4	121·9	0·95	93·8	1·48	0·57							
,, ,, ,, II.	0·9703	190·5	126·5	0·0	...	1·53	1·8							
Thick ,, ,, I.	0·9720	190·0	109·4	0·24	94·68	6·36	1·45	9·17	5·12	1·65	113·53	32·31	130·4	106·43
,, ,, ,, II.	0·9747	193·7	118·5	0·0	95·6	0·36	0·25							
Burnt ,,	0·9912	178·6	102·69	0·0	93·53	9·12	1·14							

[1] There was no colophony present.

[2] Determined by the lead-salt-ether method.

The following table due to *de Waele*[1] illustrates the course of polymerisation in an oil kept out of contact with air. The oil (a Baltic oil) was heated in an atmosphere of carbon dioxide at 250° C. :—

	Raw Oil.	12 Hours.	56 Hours.	77 Hours (solid).
Specific gravity at 15·5° C.	·9351	·9423	·9664	...
Refractive index at 25° C.	1·4808	1·4835	1·4936 (15° C.)	1·4790 17·5° C.
Iodine value	196·6	175·2	119·8	...
Oxidised acids, per cent	0·78	0·29	0·5	3·24
Saponification value	...	...	190·7	186·0
Solid acids[2]	5·25	7·03	...	48·8
Iodine value of solid acids	17·5	...	...	86·4

There was a notable increase in the proportion of "solid acids"; they were, however, transparent and of a gummy consistence. By boiling the products obtained after 77 hours with amyl alcohol, *de Waele* obtained an extremely tough, insoluble residue which had an iodine value of 94. This residue was very resistant to the action of alkalis. This observer believes it to be a closed chain compound, and proposes for it the name of "cyclolin." A similar product obtained by *H. Ingle and A. Woodmansey*[3] is termed by them "polyolin"—as the residue left on extracting a gelatinised oil with ether had the iodine value 53. On saponification it yielded 45 per cent of fatty acids insoluble in petroleum ether, 45 per cent of fatty acids soluble in petroleum ether, 4·7 per cent of ash, and 5·3 per cent of glycerol.

The fatty acids insoluble in petroleum ether had the mean combining weight of 348·4.

The numbers recorded in the foregoing tables show in a general way (considering that we have to deal with commercial products) that the glyceridic part of the oil has not undergone destruction, and that the higher the temperature to which the heating is carried, the greater is the specific gravity. Apparently the amount of oxidised acids increases in proportion to the specific gravity. The irregularities in their percentage numbers prove, however, that the proportion of oxidised acids depends on the access of air during the boiling, and the conclusion must therefore be drawn that, if access of air were excluded entirely, practically no oxidised acids would be formed. The numbers given in the column "yield of ether-insoluble bromides" show that during the process of heating the linolenic acids are polymerised first. This is confirmed by the work of *R. S. Murrell*,[4] who showed that by heating linseed oil in an atmosphere of carbon dioxide to a temperature below that at which gelatinisation takes place (260°-280° C.) it could be separated into two factions by means of acetone, both of which, however, were soluble in low boiling petroleum ether. From its resemblance to polymerised poppy seed oil it is concluded that the acetone soluble portion contains the bulk of the linolic acids. Since it was observed that the iodine value of the polymerised oils increased with the time the solution was allowed to act—due no doubt to the gradual opening out of the polymerised molecule—it is evident that the condensation takes place in the double linkages. That some migration of the double linkages occurs during polymerisation is deduced by *Murrell* from the solubility of the lead and barium salts of the fatty acids. The characteristics of a linseed oil heated to 260° to 280° C. in an atmosphere of carbon dioxide for 28 to 60 hours, together with the figures for the portions soluble and insoluble in acetone derived therefrom, are given in the table below :—

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[1] Private communication.

[2] Fachini and Dorta's acetone method.

[3] *Journ. Soc. Chem. Ind.*, 1919, 101 T.

[4] *Journ. Soc. Chem. Ind.*, 1915, 105. Cp. also H. Wolff, *Kolloid Zeits.*, 1920, 27, 183.

	Raw Oil.	Thickened Oil.	Insoluble in Acetone.	Soluble in Acetone.
Specific gravity . .	0·933	0·969	0·9763	0·9527
Refractive index at 19° C.	1·4831	1·4915	1·4964	1·4846
Acid value	0·4	1·7	0·2	7·5
Saponification value .	197-203	200-203	190-204	193
Iodine value . .	185	118-134	97-121	92-143
Glycerol, per cent .	9·62	10·4	...	...
Molecular weight in benzene	805	1686-1704	1788-2517	904-975

The considerable iodine values which the lithographic varnishes still exhibit may be explained by the assumption that the glycerides of linolic acid have remained intact to a large extent. Thus the bromide test (in addition to the specific gravity test) is of great importance in the differentiation of lithographic varnishes from linseed oil.[1]

The drying power of linseed oil diminishes with the rise of the temperature in the boiling process. Thus, whereas "thin" lithographic varnishes dry approximately as well as raw linseed oil does, the "extra strong" varnish and burnt varnish dry more slowly at the ordinary temperature than does raw oil.

The examination of the polymerised oils should include the quantitative determination of the unsaponifiable matter, since tar oils and petroleum oils are largely used as adulterants. A specially prepared tar oil is sold for this purpose, under the trade name "sharp oil." Cheap printing-inks—for newspapers—contain rosin and rosin oil; printing-inks for books should consist of linseed oil only.

Polymerised linseed oils are largely used in the preparation of plastic masses,[2] artificial wood,[3] and similar substances; the function of the polymerised oils being to act as a cement or binding agent, either alone or in conjunction with rosin and other cementitious substances, for fibrous or inert material. A preparation consisting of polymerised oil, paraffin wax, and rosin has been patented[1] as a substitute for brewer's pitch. For polymerised oil used in the manufacture of linoleum (" corticine ") see " Oxidised Oils " (below).

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[1] Lewkowitsch, *Analyst*, 1904, 2.

[2] Cp. *e.g.* German patent 201,966; Chem. Fab. Liegnitz, Meusel, and Co.; Mihalik, German patent 233,780; German patent 216,605.

[3] German patent 203,367.

(2) Polymerised Tung Oil

It has been shown above (Vol. II. Chap. XIV. " Tung Oil ") that on heating tung oil to 180° C. for two hours, or to 250° C. for a shorter time, a jelly-like mass is produced. As this product is obtained whilst air is excluded, its formation must be ascribed to polymerisation, pending a better explanation. On standing, this mass becomes solid, so that it can be disintegrated to a coarse powder. The examination of a powdered mass prepared in the author's laboratory led to the following result; the corresponding numbers of the original oil are added :—

Polymerised Tung Oil (Lewkowitsch)

	Saponification Value.	Iodine Value.	Unsaponifiable Matter.
Original tung oil . .	193	163	...
Polymerised tung oil .	205·2	107·7	2·20

Nash[2] found the saponification value of a sample of polymerised tung oil lower than that of the original oil. The explanation must be found in the differences of temperature, kept up during the polymerising process, causing condensation of the carboxyl group.

W. Norman[3] observed in some experiments that the saponification value of the polymerised oil was lower than that of the original, whereas in other experiments, when the temperature reached 300°-320° C., the saponification value of the solidified oil was higher than that of the original oil. In the latter case the iodine value of the fatty acids had fallen to 68. From a tung oil prepared in an atmosphere of carbon dioxide, *de Waele*[4] isolated a body insoluble in amyl alcohol which he termed " cyclostearin " (cp. p. 135). This body had the iodine value 27·4. *R. S. Murrell*[5] polymerised tung oil in an atmosphere of carbon dioxide, stopping the reaction while the oil was still soluble in low boiling petroleum ether. The polymerised oil was only partially soluble in acetone (cp. p. 135). The following figures were recorded :—

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[1] German patent 203,795.
[2] Private communication.
[3] *Chem. Zeit.*, 1907, 188.
[4] Private communication.
[5] *Journ. Soc. Chem. Ind.*, 1915, 105.

[Table

	Raw Oil.	Thickened Oil.	Insoluble in Acetone.	Soluble in Acetone.
Specific gravity . .	0·9405	0·956	...	0·9542
Refractive index .	1·5172	1·5134	...	1·5114
Acid value . . .	3·3	2·3	...	2·47
Saponification value .	192-194	190-201	198·5	192·6
Iodine value . .	165-168	143-171	76·5-151	93-157
Glycerol per cent .	10·47	8·3	...	...
Molecular weight in benzene . . .	797	1431	...	876·2

Meister[1] examined polymerised tung oil after exposure in a thin layer on a glass plate. The results are given in the following table:—

	Original Oil.		After 2 Hours.		After 4 Hours.	
	I.	II.	I.	II.	I.	II.
Iodine value	148·8	144·9	143·1	138·9	...	...
Increase in weight per cent .	...	...	0·9	0·6	4·2	5·0

No absorption of oxygen takes place during the process of polymerisation, and hence no increase in weight is observed. A comparative determination by the boiling point method (in benzene) showed that the mean molecular weights of the fatty acids of the polymerised tung oils had risen to the mean values 554-809, the mean molecular weight of the fatty acids of the original oil being 399-441.

The following table shows the influence of heating on the specific gravity. For the purposes of the test the oils were heated rapidly in wide-mouthed flasks to the temperatures stated (cp. Vol. II. p. 85):—

°C.	Japanese.	Chinese.	
Original oil	0·93386	0·9412	0·9419
213	0·9349	0·9428	0·9432
232	0·9355	0·9445	0·9441
250	0·9477	0·9448	0·9504
300	...	0·9592	Solidified
310	0·9553	0·9638	...
320	0·9650	0·9700	...
330	0·9694	Solidified to a jelly	...
340	0·9760		...

A satisfactory technical application of polymerised tung oil has not yet been found, although its semi-elastic properties, and its apparent resistance to air, moisture, etc., suggest its employment as a substitute for solidified linseed oil (see below). A number of patents[2] have been taken out for processes purporting to produce varnishes (mixtures of polymerised tung oil with gum-resins) from polymerised tung oil alone, or from mixtures of polymerised tung oil with linseed oil. The manufacture of linoleum from polymerised tung oil and solidified linseed oil has also been patented.[1] The use of polymerised tung oil has also been proposed for the production of plastic masses.[2]

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[1] *Chem. Revue*, 1910, 150, and 1911, 1.

[2] Cp. Kronstein, English patents 17,378, 1900; 1386, 1901; 1387, 1901; 2679, 1901. German patents 170,788 (this patent has been declared null and void, but Dr. Kronstein appealed to the Reichsgericht), 180,621, 204,398; Cohn, German patent 257,601; Chem. Tech. Lab. Meffert, German patent 211,405.

The polymerisation of tung oil can also be effected by treatment with sulphuric acid of specific gravity 1·597-1·759, the most suitable acid being one of the specific gravity 1·688. For the preparation of the polymerised oil one part of tung oil is gradually mixed in the cold with 0·26 parts of sulphuric acid of specific gravity 1·688. The mass is stirred frequently and allowed to solidify by standing. It is then thrown into water and allowed to remain therein, until the mass has become powdery and almost white ; next it is ground and washed with water until all the sulphuric acid has been removed. The powder is finally freed from water by pressing, and dried by exposure to the air. The mass so obtained is stated to be serviceable [3] as an india-rubber substitute, insulating mass, etc. It should be added that the resulting product is free from sulphur. *Winkler* [4] heats a mixture of Chinese tung oil, phenol, and castor oil under pressure to 300° C. The product is stated to be highly resistant to acids, alkalis, and organic solvents, and also to possess a good insulating capacity. By saponifying the polymerised oil and treating the resulting soap with an acid an oily mass is obtained which is said to be useful as a substitute for polymerised linseed oil (owing to its solubility in alcohol), and as a substitute in the manufacture of lacquers, etc.

(3) POLYMERISED SAFFLOWER OIL

The pronounced drying properties of safflower oil suggested the likelihood that this oil also would become polymerised under the same conditions as does linseed oil. Experiments carried out in the author's laboratory have proved this to be the case. The numbers obtained are given in the following table, in which the original safflower oil is contrasted with its polymerisation products, and with the native product "roghan" (Afridi wax), the manufacture of which has been described in Vol. II. Chapter XIV. p. 110 :—

	Specific Gravity.	Iodine Value.
Safflower oil	0·9274	147·3
,, ,, heated to 300° C. for 2 hours .	0·92938	143·4
,, ,, ,, ,, 4 ,,	0·93077	142·7
,, ,, ,, ,, 6 ,,	0·93949	121·7
,, ,, burnt 6 minutes . . .	0·95481	99·3
,, ,, Indian "distilled" oil ("roghan," Afridi wax)	0·9638	121·8

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[1] English patent 5789, 1903, Dewar and Linoleum Manufacturing Co.

[2] Lilienfeld, French patent 417,392 ; German patents 246,443, 259,840.

[3] German patent 200,746 (F. Steinitzer).

[4] German patent 247,373.

(4) POLYMERISED CASTOR OIL

The changes which castor oil undergoes on being subjected to destructive distillation have been described (Vol. II. p. 413). It has further been shown that if the distillation of castor oil be stopped just before the mass is converted into an india-rubber-like substance, the oily residue still contains glycerides.

With a view to following the changes more closely which castor oil undergoes, the author heated the oil rapidly to 200°, 250°, 300°, and 350° C. in an open dish and determined the iodine values of the products obtained.

Polymerisation of Castor Oil on heating (*Lewkowitsch*)

	Iodine Value.
Original castor oil	83·0
„ „ after heating rapidly to 200° C.	87·03
„ „ „ „ 250° C.	89·28
„ „ „ „ 300° C.	90·19
„ „ „ „ 350° C.	93·72

Fendler [1] examined a product manufactured on a commercial scale [2] by heating castor oil to 300° C., until about 5 per cent of its weight has distilled over in one hour. The product had the following characteristics:—

Specific gravity at 15° C.	0·9505
Saponification value	191·8
Iodine value	101·0
Acetyl value	67·4

From the iodine number it follows that the polymerisation has not affected the unsaturated carbon atoms. The increase in the iodine value, and the considerable decrease of the acetyl value, as contrasted with the corresponding numbers of original castor oil, prove that the polymerisation has taken place in the first instance in the direction of the formation of glycerides of di-, tri-, tetra-, and penta-ricinoleic acids, which in their turn became converted into the glyceride of triundecylenic acid (cp. "Turkey-red Oil," below).

The polymerised oil differs from the original castor oil in that it is almost insoluble in absolute alcohol, as also in 90 per cent alcohol and in acetic acid, whereas it is miscible with mineral oils in every proportion, and forms an emulsion with water; this emulsion separates, however, after a short time into two layers. The product is most likely a mixture of glycerides of undecylenic acid (see Vol. II. p. 413) and glycerides of polymerised ricinoleic acids.

The *Stern-Sonneborn* Company [3] avoid the loss of material occurring in the process described above by heating castor oil under pressure in an autoclave. The best conditions for carrying out the process are obtained by heating castor oil under a pressure of 4-6 atmospheres for 10 hours at a temperature of 260-300° C. The product is then miscible with mineral oil in all proportions. A modification of this process [1] consists in heating the castor oil under ordinary pressure under a reflux condenser.

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[1] *Berichte d. D. Pharm. Gesellschaft*, 1904, 135.

[2] German patent 104,499, Chemische Fabrik Flörsheim, Dr. H. Nördlinger; the product is sold under the fancy name "Floricin."

[3] French patent 350,511; English patent 24,935, 1905; 24,936, 1905.

Another method of converting castor oil into a polymerised product consists in treating the oil with a concentrated solution of zinc chloride,[2] or with the fused hydrated crystallised salt. The product obtained is a horny mass, which may be freed from zinc chloride by washing with water. The degree of solidification (polymerisation) depends on the proportion of zinc chloride used, its concentration, and the temperature employed. This product was proposed to be used as a covering and insulating mass. Very likely it is identical with the elastic, horny mass left in the retort on heating castor oil until the residue is suddenly converted into the solid mass described Vol. II. p. 414.

Hitherto this product does not appear to have been employed in the arts.

In addition to zinc chloride also aluminium chloride has been proposed and patented as a polymerising [3] (condensing) agent.

(5) Polymerised Sterculia Oil

It has been shown above (Vol. II. p. 389) that sterculia oil on heating becomes polymerised to a jelly-like mass. A specimen of this polymerised mass, prepared in the author's [4] laboratory, was found to be insoluble in alcohol, ether, carbon tetrachloride, chloroform, and glacial acetic acid. The following numbers were determined :—

Characteristics of Polymerised Sterculia Oil (Lewkowitsch)

Saponification value	184·9-184·5
Iodine value [5]	76·0-76·3
Unsaponifiable matter	1·16 per cent

Wedemeyer [6] heats the oil rapidly to about 200° C. and then slowly to about 250. In order to prevent the oil catching fire owing to the spontaneous evolution of heat (cp. Vol. II. p. 389) cold water is sent through a worm immersed in the oil, and also, if necessary, sprayed on the surface of the oil. *Wedemeyer* proposes the use of polymerised sterculia oil as a substitute for india-rubber.[7]

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[1] Addition to French patent 350,511, No. 4313.

[2] C. E. Alder Wright, *Journ. Soc. Chem. Ind.*, 1887, 326. This method has been patented recently by C. Dreymann, French patent 377,262, 1907.

[3] Akselrod, German patent 150,882, 1904, patented again by C. Dreymann, French patent 377,262, 1907.

[4] Unpublished observations.

[5] The iodine value was determined by warming the substance for a few minutes with the Wijs iodine solution, and allowing the mixture to stand for one hour.

[6] German patent 211,043.

[7] German patent 211,030.

IV.—BOILED OILS

French—*Huile cuite.* German—*Gekochtes Leinöl, Leinölfirnis.*
Italian—*Olio cotto.*

The oils described under this head take their name from the almost obsolete process of heating linseed oil, mixed with a small quantity of suitable metallic oxides or metallic salts—*driers, siccatives*—over free fire to temperatures varying from 210° to 260° C.

This process was termed " oil boiling." Up till recently this industry had remained a truly empirical one, and was carried on much in the same fashion as it was practised by its inventor, the Dutch painter, *Jan v. Eyck.*[1] It was found that linseed oil, after heating with lead oxide, absorbed oxygen more rapidly than did linseed oil not so prepared, and whereas raw linseed oil requires about three days for drying to an elastic skin, the drying process is so much accelerated by the treatment with lead oxide over free fire that linseed oil so treated will dry even within six to eight hours to an elastic skin.

What action takes place during the process of boiling is not yet fully known. A slight decomposition of the glycerides undoubtedly occurs, as is proved by the evolution of acroleïn vapours during the boiling; but such decomposition of the linseed oil is very limited, as the " boiled oil," like the polymerised linseed oils (lithographic varnish), still yields almost its full amount of glycerol. Moreover, practical experience has proved that boiled oils must be made from glycerides, since " boiled oils " cannot be obtained from linseed oil fatty acids, or from ethylic esters of the mixed linseed oil fatty acids.[2]

Whilst the oil is under the influence of the high temperature, polymerisation will occur to some extent (see p. 131). No hydrocarbons (due to destructive distillation) are formed, or, at any rate, not to an appreciable extent, as is proved by the small amounts of unsaponifiable matter found in commercial boiled oils (cp. table, p. 154).

For a long time the view was held that the oil became oxidised, although even in the antiquated process of boiling over free fire it was kept covered and almost wholly protected from contact with air. The explanation that the metallic oxides act as oxygen carriers during the process of boiling (an assumption which seemed to find support in the fact that a number of boiled oils had low iodine values) is equally unfounded. For it will be seen from the numbers given below that " boiled oils " can be prepared having iodine values lying very little below that yielded by a normal raw linseed oil.

The older processes of boiling with " driers " [3] appears to be an empirical way of producing metal salts (lead salts or manganese salts) of the fatty acids of the boiled oils, partial saponification of the glycerides taking place at the high temperature to which the oils were subjected whilst being boiled. These lead salts (or manganese salts) of the fatty acids are able to act as oxygen carriers in the process of "drying," when the boiled oils are exposed to the atmosphere, either in their original state or in admixture with pigments, gum-resins, etc. This would lead to the explanation that the driers act as catalysts, a small quantity only being required to accelerate the oxidation (*Lewkowitsch* [1]) when the oils dry to a skin (see below). Cp. also *L. Wise and R. Duncan.*[2]

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[1] According to some writers the monk Theophilus is credited with having discovered the fact that by boiling linseed oil with lead oxide a more rapidly drying oil than linseed oil is obtained. Some writers state that Dioscorides was acquainted with the oil-boiling process.

[2] Cp. *Liebig's Annal.*, 1840, 33, 114; Henriques, *Zeits. f. angew. Chem.*, 1898, 343; also F. Boehm, Ltd., and C. A. Reihl, English patent 123,792, 1918.

[3] With regard to " Driers," cp. p. 146.

According to *Kühl* [3] the drying is due to a process of autoxidation and is accelerated in the presence of peroxides.

These views find support in the modern methods of preparing "boiled oils."

Thus at present the bulk of the "boiled oils" is obtained by heating linseed oil with driers to a temperature of about 150° C. only. The process is carried out by introducing the oil into a cylindrical vessel provided with a heating coil and agitating gear, so as to produce an intimate intermixture between oil and drier, whilst they are heated to the desired temperature. In order to increase the contact surface between oil and air and the time during which the oil is in contact with the air, *J. C. L. van der Lande* [4] places in the vessel a large number of baffles forcing thereby the air to pass through thin films of oil. The internal arrangement of a modern oil-boiling vessel [5] is illustrated by Fig. 8, the cylindrical part of the vessel having been removed to show the heating coils and the stirring apparatus. According to *Genthe* [6] the thickening of boiled oil is materially assisted if the volatile products are removed. In order to facilitate their removal, the operation is conducted in a closed vessel, the air, or indifferent gas, lying above the surface of the liquid being continuously driven through the oil by means of a suitable drum and stirring arrangement. The volatile products are condensed in the upper part of the vessel in such a manner that they cannot return to the oil.

Wilbuschewitsch [7] atomises the oil by spraying it into an autoclave, where it meets a stream of air or ozonised air. The oil may be admixed with a catalyst capable of occluding oxygen. Some manufacturers assist the "boiling" by blowing with air. The oils so obtained are known on the Continent as "blown boiled oils" (*geblasene Firnisse* [8]). These oils are unsuitable for the preparation of best varnishes.

The preparation of boiled oils under the influence of ultra-violet light (cp. "Linseed Oil," Vol. II. p. 60) (emitted from an "uviol" lamp) has been patented by *Genthe*.[1] About twenty "uviol" lamps [2] are immersed in a tank containing 1 ton of crude oil. The raw linseed oil is warmed to about 80° C., when the lamps are then started and finely divided air is pumped into the oil under a pressure equal to a water column of about 3 metres' height. The lamps are cooled by a current of air. The reaction generates sufficient heat (cp. manufacture of "Blown Oils" below) so that the source of artificial heat may then be stopped. The oil is stated to take up by this treatment about 5 per cent of oxygen. For the treating of a ton of raw oil about sixty kilowatt-hours are required. It is claimed that oils so prepared dry better than the ordinary boiled oils [3] (cp. p. 142).

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[1] "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.*, 1903, 592; cp. also Fahrion, *Zeits. f. angew. Chem.*, 1909, 722.

[2] *Journ. Ind. and Eng. Chem.*, 1915, 7, 202.

[3] *Pharm. Zentralh.*, 1910, No. 10.

[4] German patent 209,851.

[5] I am indebted to Messrs. Manlove, Alliott, and Co., Nottingham, for this illustration.

[6] English patent 16,665, 1909.

[7] English patent 15,440, 1911. Cp. also Ramage, English patent 7842, 1901.

[8] Cp. S. Lewiak, German patent 154,091; Buchanan, English patent 7646, 1905; Leppert and Ragoon, English patent 17,035, 1903; French patent 334,233; German patent 181,193 (Leppert, Rogovin, and Rudling) (boiling in vacuo or in a current of superheated steam); Noury and van der Lande, Austrian patent 46,563; French patent 392,793.

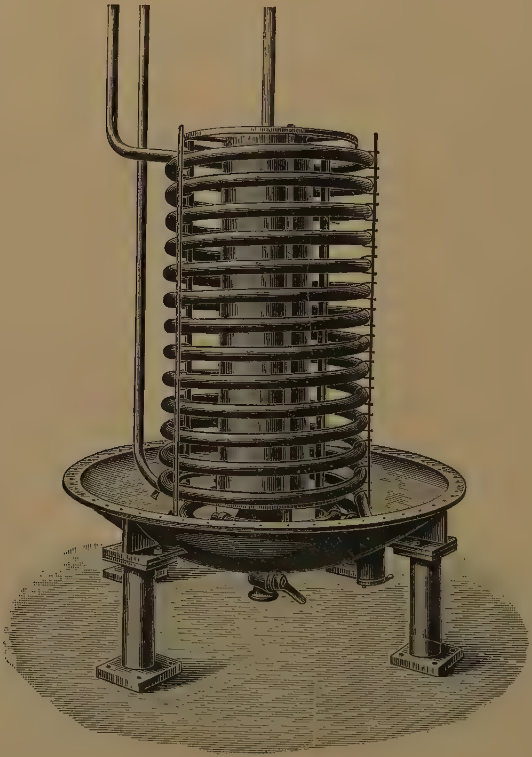

Fig. 8.

According to the quality and the amount of drier added, and the length of time during which the oil is heated ("boiled"), pale or dark oils are produced. The former are known in commerce as "pale boiled oils," the latter as "double boiled oils." The temperature can be reduced even to 120° C. by merely dissolving "liquid driers" (solutions of lead linoleate, etc., in linseed oil; see below), and assisting the operation, if required, by a current of air.[1]

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[1] German patent 195,663; cp. also German patent 223,419; Henri, Helbronner and Recklinghauser, French patent 424,369, 425,406; Banque de Radium, French patent 426,297; Nogier, French patent 426,606. With regard to the rays emitted by boiled oils, cp. W. Schmidt, *Zeits f. physik. Chem.*, 1908, (64) 243.

[2] Cp. K. Hahn, *Zeits. f. angew. Chem.*, 1908, 1442.

[3] Cp. *Chem. Zeit. Rep.*, 1908, 325.

This last process yields somewhat inferior drying oils to those obtained by boiling at 150° C. with lead oxide, etc. It has, however, been inferred therefrom that in order to obtain a quickly drying oil it suffices to prepare a solution of metal salts in oil. This view has even led to the preparation of "boiled oils" in the cold, by merely adding to linseed oil a solution of lead linoleate or manganese linoleate, and carefully intermixing it with the oil. (An oil having the properties of a "boiled" oil can also be prepared by carefully grinding linseed oil with manganese borate in the cold.) These "boiled oils" are therefore identical with the product painters used to prepare themselves from raw linseed oil by grinding it with a drier. Such oils naturally do not dry so rapidly as do the oils prepared at a higher temperature; they behave more nearly like raw linseed oil as regards the time required to "dry." From this it would follow that a certain amount of polymerisation must take place, in order to accelerate the subsequent oxidation, when the oil is allowed to "dry" (cp. below).

Raw Materials used in the Manufacture of Boiled Oils

1. **Oils.**—Linseed oil is practically the only oil that is used in the manufacture of boiled oils on a large scale. Other vegetable drying oils —like candle nut oil, safflower oil (cp. table, p. 153)—also furnish boiled oils, but their drying properties are not so good as those of boiled linseed oil, a fact which is most readily explained by stating that they contain much less linolenic acid than linseed oil does. Hence these vegetable oils, as also poppy seed oil, hemp seed oil, niger seed, and soya bean oils, must be considered as being unsuitable for the manufacture of boiled oils, and the same may be said of tung oil. Perilla oil, however, although it cannot be used in its raw state owing to its peculiar property of forming drops on a painted surface, may, in conjunction with a suitable drier form a satisfactory substitute for boiled linseed oil. Lead and manganese driers are unsuitable for this oil; cobalt driers, however, cause the oil to dry with a good gloss and also inhibit the formation of oily drops[2] (cp. Vol. II. p. 43). Fish and blubber oils are less suitable for the preparation of boiled oils, owing to the fact that the glycerides of linolenic acid seem to be entirely absent, the high iodine absorptions of these oils being due to the presence of clupanodonic acid. The statements made in patent specifications as to the usefulness of these oils, either as such or in admixture with linseed oil, must therefore be accepted with reserve. *Waentig*,[3] for example, claims by heating fish oil to 240° C. and passing through the oil steam superheated to

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[1] Cp. Hartley and Blenkinsop, English patent 11,629, 1890.

[2] Rosenthal, *Farbenzeit.*, 17, 739.

[3] German patent 272,465.

400° C. for twenty-five hours, to produce an oil containing only the polymerised glycerides of the unsaturated fatty acids and superior in its drying properties to linseed oil. Menhaden oil is, however, better than whale or liver oils, and an oil prepared from 70 per cent of menhaden oil and 30 per cent of linseed oil gave, according to *Toch*,[1] an extremely durable coat. The use of distillation products of tar oil (leinin) [2] and petroleum products requires further investigation.

The suitability of a raw linseed oil for making " boiled oil " was hitherto determined in practice by its age. It is well known that fresh oils (" green " oils), owing to traces of dissolved water, etc., give a scum on boiling, and effervesce strongly, whereas old " tanked " oils, from which water and " mucilage " have settled out on storing—" tanking "—yield the best boiled oil. A practical test for judging its suitability is to heat the oil rapidly in a test-tube to about 300° C. A suitable oil remains clear, whereas from a " green " oil, or an insufficiently refined oil, " mucilage " separates out (cp. Chap. XIV. p. 59). The observations made by *Thompson* (Vol. II. p. 59) prove that the " mucilage " is due to the presence of inorganic salts, which settle out from a " tanked " oil in course of time, carrying down with them organic impurities left in the oil. Further proof for the correctness of this view is given by the fact that these impurities are removed by refining raw linseed oil with sulphuric acid, or by cooling, or by rapid heating followed by rapid cooling. Other tests for purity have been given already under the heading " Linseed Oil " (Vol. II. p. 65). Practical experience has shown that Baltic oil is better for the manufacture of boiled oil than is Indian oil; this is readily explained by the greater purity of the Baltic seed. But Indian oil and even La Plata oil, if carefully prepared from cleaned seeds, yield oils equally as good as Baltic oil. Cold pressed linseed oil is better than hot pressed; this finds its explanation in the fact that the cold pressed oils contain smaller amounts of solid glycerides than do the hot pressed.

With a view to removing the bulk of the solid glycerides from linseed oil, as they obviously diminish the drying property of the oil, the author tried on a large scale to separate the solid glycerides by the process of " demargarination," viz. by cooling the linseed oil to −25° C. This process (for which a provisional patent only was taken) has been abandoned as unremunerative.[3]

2. **Driers** (in the United States also termed " Japans ").[4]—In the older processes of oil boiling only the oxides of lead and manganese,[5] such as litharge, red lead, manganese dioxide, or their inorganic salts, were used as driers; zinc,[6] copper, and iron salts were found incapable

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[1] *Oil and Colour Trades Journ.*, 1913, 44.

[2] *Farbenzeit.*, 1910, 2120.

[3] Cp. Lewkowitsch, *Jahrbuch der Chemie*, 1902 (xii.), 370. The same process has been patented by Hertkorn, German patents 129, 809, 137,306; cp. A. Kronstein, German patent 204,398.

[4] Cp. Weger, *Zeits. f. angew. Chem.*, 1896, 531; 1897, 401, 542, 560.

[5] It appears that manganese was first suggested by Michael Faraday.

[6] Cp. *Thorp. Technology Quart.* 3, 9; cp., however, French patent 332,788 (*Soc. Bonneville, et Cie*). Regarding other metals, cp. Meister, *Farbenzeit.*, 1908, 153.

of imparting to the oils the desired properties. The rosinates of chromium and nickel were also found to be unsuitable. More recently acetate, oxalate, and borate of manganese have been employed. Salts of cobalt with fatty and rosin acids have also been used with success, and are stated to be the most suitable driers for use with fish and blubber oils and perilla oil.[1] (Cp. Vol. II. p. 426.) Oils prepared with lead as drier are stated to give, on standing, more of a precipitate than manganese oils. According to *Davidson*,[2] this precipitate consists of the lead salts of the saturated fatty acids, as this observer found, for the fatty acids prepared from a precipitate containing 30·1 per cent lead oxide, the iodine value 4·6. As rosin is capable of absorbing oxygen from the air, the metallic salts of the rosin acids [3] have also come into vogue as driers. Lead rosinate is, however, falling into disfavour on account of its property of sometimes causing cloudiness in the varnish (*de Waele*). Rosinates are prepared either by precipitating a (soda) soap solution with solutions of metallic salts (*e.g.* sodium rosinate with manganese sulphate), or are simply synthesised by fusing together a metallic oxide with colophony; hence there are discerned in commerce "precipitated" driers and "fused" driers.

By precipitating rosin soap solutions, or by fusing colophony, as the case may be, with mixed manganese and lead salts, "precipitated" or "fused" *mangano-lead driers* are obtained.

A ready method of distinguishing "precipitated" driers from "fused" driers is afforded by the determination of water. Only the "precipitated" driers contain notable quantities of moisture (up to 6 per cent).

A further development in the industry of driers was reached by the employment of the metallic salts of linseed oil fatty acids. These salts are prepared either by precipitating soap solutions obtained by saponifying linseed oil with solutions of metallic salts, or by heating the fatty acids together with oxides. Thus "precipitated" manganese linoleate, lead linoleate, etc., or "fused" manganese linoleate, etc., are obtained.

By means of these methods the author prepared driers from *tung oil*. Thus a lead tungate, manganese tungate, and a mixture of the two—lead-mangano-tungate—were manufactured on a large scale.

The driers prepared from linseed oil fatty acids, tung oil fatty acids, and rosin (colophony) are soluble in "oil of turps" (turpentine oil), ether, chloroform, and linseed oil,[4] and are therefore termed "soluble driers." Solutions of these driers in linseed oil or in turpentine oil or in a mixture of both are obtainable in commerce under the names "liquid driers," "terebene,"[5] and other fancy names.

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[1] Krauss, *VIII. Int. Cong. Appl. Chem.*, 1912, Sect. V^e. p. 127; Fokin, *Zeits. f. angew. Chem.*, 1909, 1451, 1492.

[2] *Oil and Colour Trades Journ.*, 1908, 1588.

[3] With regard to driers from copals—"copal resinates"—cp. Bottler, *Dingl. Polyt. Journ.*, 1898, 70.

[4] It should be noted that the solubility of "linoleates" and rosinates in ether or chloroform in the cold exactly coincides with their solubility in linseed oil at somewhat elevated temperatures—up to 120° C. Cp. Lippert, *Zeits. f. angew. Chem.*, 1903, 366.

[5] Cp. Fawsitt, *Journ. Soc. Chem. Ind.*, 1903, 538; Coste and Andrews, *Analyst*, 1910, 154.

The examination of driers consisting of metallic oxides or of metallic salts of inorganic acids is carried out by the well-known methods of mineral analysis.[1] The valuation of the "soluble driers" cannot be based on the proportion of the metal, as determined by incineration, inasmuch as the oxides held in suspension, and therefore not chemically combined with fatty acids or rosin acids, are not only useless to the manufacturer of boiled oil, but are even injurious, as they render the oil turbid. A preliminary test consists in treating the drier with organic solvents. A good drier should dissolve completely in ether, or, in the case of lead rosinate, in chloroform and in turpentine oil.

In the analytical examination of a soluble drier the organic matter is first burnt off in a porcelain crucible, and the amount of total lead, manganese, etc., is determined in the ash. The weight of the ash does not always give useful indications, as the fused driers often contain sand, etc. In addition to lead and manganese, the calcium in the ash may be determined. (Calcium rosinate is a legitimate constituent of driers.) A fresh portion of the sample is then extracted with ether or chloroform or turpentine oil. From the filtered solution the solvent is evaporated off and the residue incinerated. In the ash, the lead or manganese, or both (as the case may be), are determined quantitatively, and the difference between the lead or manganese found in this experiment and that found in the first experiment corresponds to the amount of lead or manganese present as insoluble excess. The result may be checked by determining the dissolved lead or manganese in an aliquot portion of the solution. In the case of a rosinate the dissolved lead must be determined by difference, as the chloroform is stated to be only driven off completely from the rosinate at a red heat, when a portion of the lead also volatilises as chloride. The amount of metal in some driers is given by *L. Radcliffe and C. Palmer*[2] whose results are reproduced below :—

Metallic Rosinate.	Percentage of Metal in			
	Precipitated Drier.		Fused Drier.	
Zinc	7·7		3·6	
Calcium	4·6		3·0	
Copper	7·8		...	
Magnesium	5·1		0·7	
Manganese	3·5		2·3	
Lead	15·2		16·7	
Cobalt	...		2·4	
	Mn.	Pb.	Mn.	Pb.
Manganese lead	2·3	10·8	1·13	7·2

It should be noted that the precipitated drier contains water whereas the fused drier is anhydrous.

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[1] With regard to the analysis of manganese borate, cp. Endemann and Paisley, *Amer. Chem. Journ.*, 1903, 68.

[2] *Journ. Soc. Chem. Ind.*, 1915, 644.

Corresponding figures for the metallic salts of linseed oil fatty acids are also given :—

Metallic Linoleate.	Percentage of Metal.
Manganese	9·4
Lead	25·8
Copper	7·7
Aluminium	4·3
Cobalt	9·5
Zinc	9·0
Calcium	8·3
Magnesium	3·4

The fatty acids or rosin acids, although their examination is of minor importance, may be determined by decomposing the ethereal solution with mineral acid.

The following is the analysis of a commercial drier carried out by the author :—

	Per cent.
Ash	18·6
Fatty acids, including rosin acids	83·42

The more detailed examination gave the following result :—

Complete Analysis of a Commercial Drier (*Lewkowitsch*)

	Per cent.
Lead oxide	10·99
Manganous oxide	6·79
Iron peroxide	0·47
Calcium oxide	0·56
Rosin acids	38·32
Oxidised acids	4·24
Other fatty acids	40·86

It must, however, be understood that the results furnished by a chemical analysis alone are not sufficient to supply the data on which an opinion can be based as to the properties the drier will impart to the oil. The colour and drying power of the boiled oil to be prepared, and other conditions, greatly influence the choice and quantity of the drier.

Soya bean oil is stated by *Gardner*[1] to dry best with a linoleate drier when the content of metals is manganese 0·03 per cent, lead 0·20 per cent, and cobalt 0·01 per cent.

The cerium salt of linseed oil fatty acids is stated by *R. S. Murrell*[2] to be superior to the corresponding lead salt.

A table detailing the proportions of metal contained in some commercial driers, as also the minimum temperatures at which they may be used, is given in the author's *Laboratory Companion to the Fats and Oils Industries*.[3]

Each manufacturer appears to have his own "formula" for the quantity and composition of driers he adds to the oil in the boiling process. These "formulæ" are guarded by the makers as valuable secrets. As a rule, a quantity of driers not exceeding 2 to 3 per cent of the oil is added. According to a recommendation of the *Deutsch Schutzverein für Lack- und Farbenindustrie*[1] a pure linseed oil varnish must not contain more than 2 per cent of drier, or, if rosin driers are used, not more than 5 per cent of rosin acids. The best results are stated by *Weger* to be obtained by using a mangano-lead drier, the manganese and lead salts being mixed in such proportions that the metallic lead (Pb) and metallic manganese (Mn) are present in the proportion of 5 to 1. The production of a drier by heating a mixture of aluminium hydrate and aluminium acetate in rosin and then adding sufficient soda to neutralise the rosin acids has been patented.[2]

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[1] Circular No. 69, Paint Manufacturers' Association of the U.S., 1919.

[2] *Chem. Soc. Trans.*, 1918, 113, 111.

[3] Table No. 43, p. 84. Analyses of inferior commercial driers have been given by Coste and Andrews, *Analyst*, 1910, 155.

The solid driers have the drawback that a considerable amount of "foots" settles out from the stored finished product.[3] No such deposit is formed when liquid driers are employed.

The drying power of finished boiled oil depends to a certain extent only on the quantity of drier added. When a given amount of drier has been incorporated with the oil, its drying power is not increased by a further addition of drier; in some cases the drying power actually decreases. Thus *Weger* states that the time necessary for drying to an elastic skin is the shortest when the boiled oil contains 0·2 per cent of manganese as metal, and in the case of mangano-lead driers 0·6 per cent of metals, the proportion of lead to manganese being 5 to 1.[4]

Lippert[5] pointed out the differences which the boiled oil skins show according as to whether they are prepared with lead driers or manganese driers. Whilst the boiled oils containing lead dry to a leather-like skin, the oils prepared with manganese are more brittle and harder. As long as the boiled oils prepared with lead oxide driers are kept carefully protected from access of air, they do not suffer loss in drying power; nor does the moisture of the air exercise the same influence on boiled oils prepared with lead oxide as on boiled oils prepared with manganese driers, for, in some cases, the boiled oils prepared with the aid of lead driers dry better in moist than in dry air. *Lippert* is therefore led to the conclusion that in contradistinction to boiled oils prepared with manganese the oils "boiled" with lead driers are influenced to a small degree only by the moisture of the air, and this in a manner perfectly independent of the proportion of lead. Yet, as a rule, if the air is dry, the *incipient* drying process proceeds more quickly.

Since boiled oils prepared with the aid of lead have a tendency to deposit "foots," *Lippert* tried to prevent their separation[6] by using lead rosinate, and found that "fused" lead rosinate is preferable to "precipitated" lead rosinate. Old boiled oils, rich in manganese, which frequently showed a considerable retardation in the incipient stage of drying if exposed to moist air, gained good drying properties after admixture with a lead-oxide boiled oil. These observations, taken in conjunction with the results obtained by *Weger*, show why manufacturers of boiled oil (notably in Germany) are in favour of preparing their boiled oils with the aid of lead-mangano driers. *Lippert* has further shown [1] that whilst all boiled oils dry more rapidly in a completely dry than in a moist atmosphere—without regard to the age of the oil—small quantities of manganese suffice to induce a better drying in a moist than in a dry atmosphere.[2]

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[1] *Zeits. f. angew. Chem.*, 1912, 876.

[2] Pilgram and Leffer, French patent 399,804.

[3] W. Traine (German patent 161,941) suggests the use of lime as a means of preventing the formation of "foots." Since calcium rosinate is frequently used as a "drier," there is no novelty in the claim.

[4] *Zeits. f. angew. Chem.*, 1897, 401, 524, 560; *Die Sauerstoffaufnahme der Öle und Harze*, E. Baldamus, Leipzig (cp. Lippert, *Zeits. f. angew. Chem.*, 1897, 655; 1898, 412, 431; 1903, 366).

[5] *Chem. Zeit.*, 1903, 365.

[6] As to other suggested means of preventing the formation of "foots," cp. E. Täuber *Chem. Zeit.*, 1906, 1252.

In the drying of boiled oils the influence of temperature, light, and of moisture of the air plays an important part. *Lippert* [3] specially examined the influence of the last-named factor (proportion of moisture of the air) on the drying of boiled oils prepared with manganese driers, by exposing glass plates covered with a drying oil both to the ordinary atmosphere and to a completely dried atmosphere (under a desiccator). It was found that boiled oils containing over 0·05 per cent of manganese dried more quickly in dry air than in moist air. The rule appears to hold good that boiled oils rich in manganese dry more quickly in dry air than in moist air, whilst boiled oils poor in manganese dry more rapidly in moist air than in dry air.

It would appear to the author from these observations that the proportion of manganese in a boiled oil should be regulated according to the season in which it is to be used.

With regard to the theory of the action of driers, cp. p. 191.

Examination of Boiled Oils

The chemical examination of boiled oils embraces the detection of adulterants, such as fish oils, vegetable oils (other than linseed oil), mineral oils, naphthalene,[4] rosin oils, and rosin (cp. "Linseed Oil," Vol. II. p. 65). Oils prepared with liquid driers may legitimately contain small proportions of oil of turpentine. The number of "boiled oil substitutes" in the market is very large; they are mostly made up of rosin, rosin oils, tar oils, petroleum oils,[5] with a small quantity of linseed oil or tung oil, or fish and blubber oils, and must be looked upon as adulterated oils. Most of the so-called "patent boiled oils" fall under this stricture.[6] On painting an alcoholic solution of "oxidised" acids from marine animal oils on glass or wood so that a thin layer of the oxidised acids is left, they acquire on drying a lustrous, dark brown colour and so assume the appearance of a varnish (*Tsujimoto*[1]).

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[1] *Zeits. f. angew. Chem.*, 1905, 94.

[2] There is no doubt that the velocity of the reaction, *i.e.* the drying, increases rapidly with the temperature, but no proof has been furnished as yet that the velocity of reaction increases according to Spring's rule, viz. rises to double the velocity for a rise of 10° C.

[3] *Chem. Zeit.*, 1900, 133.

[4] The addition of naphthalene has been patented by W. Traine, English patent 5261, 1903.

[5] Pollard, *Analyst*, 1912, 247.

[6] The German patent 181,192 protects a substitute made from soft soap, amber varnish, drier, and water. German patent 166,563 claims wool fat and wool fat acids in conjunction with zinc rosinate. German patent 208,753 (K. Winkler) claims cod liver oil, rosin spirit, manganese rosinate.

Boiled oil is readily differentiated from raw oil by its specific gravity, by the presence of drier (giving a residue on incineration), and by the bromide test (see below). Boiled oil is frequently mixed with raw linseed oil, since boiled oil, if used alone, gives in some cases a "hard" coat liable to crack; hence the detection of raw linseed oil in boiled oils is of little practical importance in this country.

In those countries, however, where raw linseed oil and boiled oil are assessed differently by the custom-house officials, the rapid distinction of linseed oil from boiled oil is frequently required. *Finkener* recommends, for custom-house purposes, the following test, by which 25 per cent of boiled oil is stated to be detected in raw oil. The following reagents are required :—A 20 per cent ammonia solution, and a solution containing 100 grms. of lead acetate and 32 grms. of glycerin in 120 c.c. of water. The test is carried out as follows :—1 c.c. of the ammonia solution is mixed with 5 c.c. of the lead solution, 12 c.c. of the sample are added, and the whole is vigorously shaken together and then heated for three minutes to 100° C. If the sample be pure linseed oil, it will form two layers on standing, the lower one being clear, while if the sample contain boiled oil it will set to a soft, viscous mass.

The best test for the detection and approximate determination of raw linseed oil in boiled oils prepared at elevated temperatures is the bromide test.[2] The oils boiled over free fire by the old process undergo polymerisation much in the same way as do the polymerised oils (p. 131). It has been shown above that the yield of ether-insoluble bromides rapidly decreases with the temperature employed. Hence these boiled oils will give a much lower yield of bromides. In boiled oils, however, which have not been heated to such high temperatures this method would not give a decisive answer, as the oils, not having undergone polymerisation, still yield approximately the same amount of bromides as do the original oils.

This is clearly brought out by the following table, in which the iodine values of some "pale boiled" oils and some "double boiled" oils prepared at 150° C. are recorded. There is a considerable decrease in the yield of ether-insoluble bromides, coincident with a corresponding, although by no means proportionate, decrease of the iodine value. The author's view that these decreases are due to polymerisation which has taken place in consequence of the high temperature is borne out by the numbers recorded for the last three linseed oils, which were prepared by an ozone process investigated by the author. The treatment was carried out at temperatures at which polymerisation does not take place; nor would any ozonides (Vol. I. Chap. VIII.) formed remain stable. Hence the yield of ether-insoluble bromides, as also the iodine value, is little lower than that of the original oil.

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[1] *Journ. Coll. Eng. Tokyo Imp. Univ.*, 1908 (5), 199.

[2] Lewkowitsch, *Analyst*, 1904, 2.

Characteristics of Boiled Oils (Lewkowitsch)

Name.	Specific Gravity.	Iodine Value.	Ether-insoluble Bromides from Glycerides. Per cent.
Linseed oil (raw)	0·9308	186·4	24·17
Pale boiled linseed oil	0·9429	171·0	20·97
Double ,, ,, ,,	0·9449	169·96	13·03
Ozonised ,, ,,	0·9310	180·1	36·26-36·34
,, ,, ,,	0·9388	171·2	25·73
,, ,, ,,	0·9483	169·7	30·19
Safflower oil (raw)	0·92461	146·46	traces
Double boiled safflower oil	0·9340	137·3	...
Pale ,, ,, ,,	0·9360	139·1	...
,, ,, ,, ,,	0·93613	137·0	...
Double ,, ,, ,,	0·9447	141·8	none
,, ,, ,, ,,	0·95035	127·3	...

The amount of oxidised acids in boiled oils should not exceed the proportions given in the following table. *Fahrion* has drawn the conclusion (from a few experiments) that a boiled oil is the better the less oxidised acids it contains (cp. p. 193).

In the chemical examination of a boiled oil, the numbers collated in the following table may be found useful as a guide :—

Some Characteristics and Variables of Commercial Boiled Oils

Description.	Specific Gravity at 15·5° C.	Acid Value.	Saponification Value.	Insoluble Fatty Acids+ Unsaponifiable.	Iodine Value.	Unsaponifiable.	Oxidised Acids.	Ash.	Rosin Acids.	Observer.
				Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
Somewhat thin and fluid	...	13·4	...	...	101·3	...	0·5	...	...	Fahrion
Very viscid	...	24·9	...	...	77·3	...	4·1	...	...	,,
Tacky, yielding strings	...	32·6	...	...	73·7	...	7·6	...	...	,,
...	...	...	188·1-192	92-92·3 (2 samples)	145·1-157·2	0·3-0·72	...	...	...	Ulzer
...	...	...	...	...	149·7-153·4	...	...	...	...	Wild
...	...	...	...	...	...	0·43-1·71	...	...	...	Bach
Very thin	0·947	8·85	182·2	...	...	2·34	...	...	...	Williams
Thin	0·948	7·06	180·9	...	...	1·27	...	...	...	,,
Thin	0·961	12·43	179·5	...	...	2·11	...	...	...	,,
Stout	0·972	19·69	189·3	...	...	2·01	...	...	...	,,
Stout	0·982	20·89	185·6	...	...	2·04	...	...	...	,,
Very Stout	0·983	24·97	183·0	.	...	2·14	...	...	...	,,
Solid	...	14·02	193·9	...	...	2·08	...	...	...	,,
Varying in consistence in the same order, from thin to very viscous	...	4·8	188·7	...	159·0	...	...	...	...	Kitt
	...	5·2	189·1	...	100·7	...	...	...	...	,,
	...	7·8	189·1	...	95·6	...	...	...	...	,,
	...	9·5	186·6	...	83·6	...	...	...	...	,,
	...	9·1	187·2	...	79·1	...	...	...	...	,,
	...	11·7	187·2	...	76·2	...	...	...	...	,,
	...	18·8	192·3	...	71·1	...	...	...	...	,,
Double boiled oil I.	0·9493	...	191·0	...	161·0	1·9	...	...	...	Lewkowitsch
,, ,, II.	0·9595	0·98	192 3	...	...	2·1	10·04	0·68	3·89	,,
,, ,, III.	0·9621	3·00	192·8	...	...	2·53	11·73	0·42	...	
"Commercial" boiled oils, 8 samples	0·9355-0·9474	2·8-6·4	187·5-192·2	...	180·4-183·3	1·12	...	...	...	McIlhiney

It should be noted that, owing to the presence of metals in boiled oils, the determination of the iodine value leads to too high results, unless the metal be first removed by treatment with mineral acids. The error that may be committed by not following these directions is shown by the figures contained in the following table :

Iodine Values of Boiled Oils (Lewkowitsch)

Boiled Oil from	Original Oil.	Boiled Oil after Removal of Metal.
Linseed oil . .	173·3	169·7
,, ,, . .	177·2	171·1
Safflower oil . .	134·9	130·7

The valuation of a boiled oil which has been found free from adulterants must be based on "practical" tests, by exposing the oil to the action of the atmosphere in a thin layer on glass plates in the manner described Vol. I. Chap. VII., and Vol. II. under "Linseed Oil." The oil is exposed either in its original state or after admixture with pigments, such as are used in the preparation of paints. A weighed or measured amount of boiled oil is therefore intimately intermixed with a weighed amount of pigment, the mass is spread in a thin layer on a glass plate, and exposed to the atmosphere side by side with a boiled oil of known quality.

A set of different pigments may be used consisting of white lead, zinc oxide, red lead, red oxide of iron, and yellow, green, blue, and finally black pigments. Since the black pigment, which is free from metals, does not act as a catalyst, the black paint requires the longest time to dry, and therefore furnishes the severest test in judging the quality of a boiled oil. It should, however, be added that a good deal of practical experience is required to arrive at a definite opinion as to the value of a boiled oil.[1] It is recommended therefore that comparative tests with boiled oils of known quality be instituted.

Boiled oil is extensively used [2] in the preparation of **paints, varnishes,** and **enamels.**

Paints

The paints to be considered here are made by grinding together levigated pigments [3] with boiled oil in special grinding machines, until a homogeneous mass, free from gritty particles, is obtained. The admixture of sulphonated petroleum residues has been patented.[1] In most works the proportion of oil is kept as low as possible, it being left to the user to " thin " the paint with more boiled oil (and " oil of turps " if required) to the proper consistence, so that the paint can " flow " under the brush. The percentage of oil in different commercial paints lies, according to the nature of the pigments, from between 8 or 10 per cent for white lead paint to 30-40 per cent for black paints.

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[1] Cp. *Weger's* papers referred to, p. 150; Lippert, *Zeits. f. angew. Chem.*, 1900, 134; 1903, 366.

[2] With regard to plastic masses from boiled oil see German patent 162,858 (J. Staudt), and also German patent 201,966 (*Chem. Fab. Liegnitz*, Meusel and Co., "Oil and Magnesium Powder").

[3] In the manufacture of "anticorrosive" or "antifouling" paints, mercury oxide and copper salts are employed. E. Täuber, *Chem. Zeit.*, 1908, 1032; 1909, 417; "Indigoide Farbstoffe in der Verwendung als Ölfarben," A. Eibner, *Chem. Zeit.*, 1909, 229, 243, 254. Cp. also W. Schoeller and W. Schrauth, German patent 285,225, 1913, and B. Zschokke, German patent 285,708, 1914.

The chemical examination of **paints** has been briefly sketched out already (p. 67). The paint is shaken out with ether to dissolve the oil. Frequently, however, the separation of oil from pigment cannot be thus effected, and a mineral acid must be added to decompose metallic soaps and to bring the pigment into solution, in case it be soluble in acid. The ethereal layer is separated from the aqueous solution and any undissolved pigment. The undissolved portions often consist of weighting substances (termed " expanders " in the United States), such as barytes, gypsum, etc. It may be pointed out here that *Sacher* [2] states that gypsum acts on the oil catalytically, inducing drying ; in other words that it acts like a drier. After evaporating off the ether, the residual oil may be subjected to further examination. In the case of artists' paints the examination includes the identification of walnut or (and) poppy seed oils. The mineral matter is examined by the well-known methods of inorganic analysis. Heavy metals like copper, chromium,[3] and mercury form the basis of anti-fouling (anti-rusting) paints.

The more important physical examination of paints as regards their suitability for a given purpose, and especially for withstanding the action of the atmosphere,[4] falls outside the scope of this work (cp. also above). For the suitability of a paint for protecting concrete see the work of *H. A. Gardner*,[5] and also *E. Ahrens*.[6] Fire-proof paints usually contain substances which evolve ammonia at high temperatures such as magnesium ammonio-phosphate.[7]

For paints made with emulsions containing oxidised oils, cp. above, p. 116.

Varnishes—Oil Varnishes

The **varnishes** [8] to be considered here consist of a mixture of boiled oil, various gum-resins, and oil of turps. Varnishes prepared from mixtures of esters of cellulose fall outside the scope of this work,[1] as also the metallic paints, which consist of finely divided metals, *e.g.* aluminium incorporated with ethyl or amyl acetate, to which in some cases is added nitro cellulose.[2]

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[1] Walker and Sohn, German patent 228,633.

[2] *Farbenzeit.*, 1912, 1825.

[3] Friedmann, German patent 248,292 ; cp. also Deutsche Österreichische Mannesmannröhren Werke, German patent 175,631.

[4] Cp. *The Chemistry and Technology of Mixed Paints*, Maximillian Toch, New York, 1907 ; *Journ. Soc. Chem. Ind.*, 1908, 311 ; and E. Täuber, *Chem. Zeit.*, 1909, 85 ; 94.

[5] Bulletin No. 47, Paint Manufacturers' Association.

[6] *Oil and Colour Trades Journal*, 1915, 1473. Cp. also C. Ellis and A. Wells, United States patent 1,179,413, 1916.

[7] Terrisse and Coffignier, French patent 398,956 ; German patent 247,372.

[8] The so-called spirit varnishes—" lacquers "—prepared by simply dissolving gum-resins in volatile solvents—alcohol, oil of turpentine, etc.—fall outside the scope of this work ; cp. French patent 398,813.

Although the processes for manufacturing varnishes are guarded as valuable secrets, the actual amalgamation of the ingredients is a simple operation. The "art" of the manufacturer consists in the suitable selection of gum-resins, and in the manner of preparing them for "running" with oil. Most of the gum-resins must be subjected to a preliminary treatment by heating to a temperature of above 300° C. before they acquire the property of remaining dissolved in the boiled oil and in the volatile oil, which is used for the "thinning" of the non-volatile portion of a varnish. The different gum-resins lose thereby from 5 to 20 per cent of their weight.[3]

The actual temperature to which each gum-resin or mixture of gum-resins is brought up, and the length of time during which the fused mass must be kept at the desired temperature (so as to avoid "under-cooking" or "over-cooking"), have been ascertained by truly empirical and, hence, costly methods. Therefore, this part of the operations is surrounded by manufacturers with the deepest secrecy. The attempts that have been made hitherto to avoid the loss incurred in the preliminary heating of gum-resins, *e.g.* dissolving them in oil of turpentine [4] or in linseed oil under pressure,[5] have not been successful, as the dissolved gum-resin is precipitated when the oil of turpentine is added. Nor have satisfactory results been obtained by dissolving the gum-resins, without previous fusion, in benzene, chlorohydrin, toluene,[6] camphor oil, fatty acids [7] (such as palmitic acid, linseed oil fatty acids, and tung oil fatty acids), naphthalene,[8] or a mixture of naphthalene and rosin oil [9] and copal oil, oil of turpentine, terpineol [10] or amylalcohol,[11] or a mixture of the alkyl or aryl esters of phthalic acid.[12]

Although unheated gum-resins are soluble in their original state in oil of turpentine, and linseed oil itself is also soluble in this menstruum, a clear solution cannot be obtained by adding linseed oil or a solution of linseed oil in oil of turpentine to a solution of unheated gum-resins in oil of turpentine. For "varnishes" so prepared, although clear at first, become turbid as soon as the oil of turpentine commences to evaporate, linseed oil being insoluble in a concentrated solution of the gum-resins. *Livache*[1] states, however, that he obtains satisfactory varnishes without previous melting of the gum-resins by substituting for the total quantity of linseed oil required in the usual varnishes a mixture of two-fifths of that quantity of linseed oil and three-fifths of its mixed fatty acids.

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[1] French patent 445,638. For the influence of the vehicle on the anti-rusting properties of a paint, cp. M. Toch, *Journ. Soc. Chem. Ind.*, 1915, 592.

[2] Gall, French patent 398,084. For further technological information cp. Thorpe's Dictionary article "Varnish."

[3] Cp. M. A. Tixier, "Sur la théorie des vernis," *Monit. scient.*, 1906, 726.

[4] French patent 16,472, 1856 (Schützenberger).

[5] Cp. Smith, *Journ. Soc. Chem. Ind.*, 1901, 1076. Lewkowitsch, *ibid.*, 1901, 1077. Lippert, *Chem. Revue*, 1901, 177.

[6] English patent 5404, 1902.

[7] German patents 129,677, 145,388.

[8] French patent 334,107 (A. Crebert); French patent 334,300; German patent 165,008 (H. Terrisse); German patent 154,756 (Fraine). Cp. also Coffignier, *Oil and Colour Trades Journ.*, 1909, 2029.

[9] Terrisse, German patent 229,145.

[10] Tixier and Rambaud, English patent 17,135, 1903; German patent 160,791. The terpineol is obtained by allowing nitric acid to act on oil of turpentine. At present terpineol is obtained as a by-product in the manufacture of artificial camphor.

[11] Livache, *Compt. rend.*, 1908 (146), 898 and *Bull. Soc. d'Encouragement*, 1908.

[12] Hesse, German patent 227,667.

A recent patent[2] claims the dissolving of copals in petroleum or shale hydrocarbons at a pressure of 17 atmospheres.

The gum-resins are fused in an open cylindrical nickel-bottomed vessel fixed on wheels, so that the vessel can be rapidly withdrawn from the open fire, over which the mass is heated. The vapours which are evolved are allowed to escape through a chimney. In some works the temperature is carefully observed during the "running," whilst the mass is well stirred, so that no part of the gum-resin may burn on to the side of the vessel. When the mass is deemed to have been heated sufficiently, the vessel is drawn from the fire, placed in an open space (yard), and the desired quantity of linseed oil or of "boiled" oil, previously warmed, is entered into the hot gum-resin, gradually and in small quantities, so as to prevent frothing over. If raw linseed oil is used, then the "boiling" is carried out over free fire, after the addition of "driers," by bringing the vessel again into the fireplace. *Niedzielski and Bourgeois* patent the use of a solution of manganese borate in turpentine.[3]

J. Berlaimant claims the preparation of varnishes by dissolving "linoxyn" and oleo-resins (without heating them preliminarily) in amylalcohol or amylacetate.

During the melting operation the gum-resins undergo a kind of destructive distillation, and considerable amounts of irritating vapours are evolved, which if condensed would yield an oily liquid containing oxygenated substances (both acid and neutral) and consisting to a great extent of terpenes.

The product thus obtained is termed "varnish oil" (French—*huile à vernis*; German—*Lacköl*). The varnish oil is allowed to "settle out," so that "foots" may separate, or it is filtered through a filter press.[4] The filter-cloths must be freed carefully from the varnish oil—by solvents—as the woven material impregnated with the varnish oil is extremely liable to spontaneous combustion.

The varnish oil is then diluted or "thinned" with oil of turpentine ("oil of turps") to produce the commercial varnish.

The most suitable fatty oil, and practically the only one used for high-class varnishes, is linseed oil. A large number of patents have been taken out purporting to substitute successfully linseed oil by tung oil, or by mixtures of linseed oil and tung oil. In order to prevent the gelatinisation of the tung oil, the addition of naphthenic acid,[1] zinc dust,[2] sulphur and sulphides[3] has been proposed. In most of the products of this kind which the author has examined, the expensive gum-resins had been substituted by colophony (which is also capable of absorbing oxygen from the air); with regard to the oxygen absorption power of colophony, cp. Table No. 38 of the *Laboratory Companion to the Fats and Oils Industries*).

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[1] *Compt. rend.*, 1908 (146), 898.

[2] E. H. Strange and E. R. Burrell, German patent 232, 405; United States America patent 1,011,659.

[3] French patent 408,902.

[4] The German patent 189,514 (Internationale Elektra, Werke, G.m.b.H., System, Dr. Kronstein) claims a layer of common salt and of some other hygroscopic substance (such as calcium chloride magnesium chloride) as a filtering medium; cp. also Wolff, *Farbenzeit.*, 1913, 2587.

For oil of turpentine the less valuable "wood oil" and cheaper hydrocarbons, especially petroleum hydrocarbons of the same boiling point, and special fractions of rosin oil are very frequently substituted. The influence of turpentine and its substitutes on the increase in weight observed in the drying of linseed oils has been studied by *A. Woodmansey*[4] who concludes that the increase apart from the polymerised residue left by turpentine is inversely proportional to the volatility of the "thinner."

The addition of organic aromatic bases containing nitrogen, *e.g.* pyridin, chinolin, anilin, etc., to varnishes and linoleum is stated to prevent the further changes due to the influence of air and light which cause the dried coat to become hard and crack.[5]

A **complete** chemical analysis of varnishes is, in the present state of our knowledge, an extremely difficult problem.[6] Whilst the fatty oil may be more or less readily recognised, it is in some cases impossible to identify the gum-resin constituent by chemical means alone, considerable practical experience being required to supplement the purely chemical examination.[7]

The first operation in the chemical examination of a varnish is to remove the *volatile solvent*. This is done by heating 100 grms. of the varnish in a current of steam[8] until no more volatile oil comes over with the vapours.

The volume of the volatile oil is measured, and after its specific gravity has been determined the absolute weight can be calculated.

E. W. Boughton[9] distils 100 c.c. of the varnish in a current of steam, maintaining the distillation flask at 115° to 120° C. Since oil of turpentine is slightly soluble in water, a correction is made by adding to the result 0·3 grms. for each 100 c.c. of water distilled over.

By these methods a sufficient quantity of the volatile thinner is obtained to permit of its further examination.

If, however, the amount only is required, a few grms. may be spread on a glass plate and dried in a current of inert gas at about 30° C.[10]

A more rapid method, due to *A. de Waele and F. Smith*,[11] is to boil

[1] "Vernisöl," *Soc. Anon.*, German patent 253,845.

[2] Weinschenk, German patent 219,715.

[3] Beringer, German patent application B, 68,951.

[4] *Journ. Chem. Soc.*, 1917, 1253.

[5] Ostwald and Ostwald, German patent 239,289.

[6] Cp. Rebs, *Chem. Zeit. Rep.*, 1908, 435.

[7] H. Wolff, *Farbenzeit.*, 1921, **26**, 1186.

[8] Cp. McIlhiney, *Journ. Amer. Chem. Soc.*, 1895, 344.

[9] *Chem. News*, 1916, **114**, 75.

[10] A. L. Brown, *Amer. Soc.*, for Testing Materials, June 30-July 3, 1914.

[11] *Analyst*, 1917, **42**, 170, and 1918, 408.

3 or 4 grms. of the varnish with 60 c.c. of water in a small wide-mouthed flask over a free flame until all smell of the solvent has disappeared.

The flask is then cooled and the water decanted. The last traces of water are removed by warming the flask with 10 c.c. of a mixture of 3 parts of benzene and 1 part of alcohol.

If necessary this operation should be repeated twice and the residual benzene-alcohol removed in a current of carbon dioxide.

For a method of determining methyl and ethyl alcohols in spirit varnishes, see G. W. Knight and C. T. Lincoln.[1]

Volatile Portion of the Varnish

The examination of the volatile portion and its identification has during latter years become a most important part of the analysis of varnishes, since, owing to the most devastating manner in which the collection of the oleo-resin (turpentine) from the pine forests of Carolina, Georgia, and Florida has been carried on, the supply of oil of turpentine ("spirits of turpentine") had decreased considerably. Thus whilst the American output of oil of turpentine (17·5 per cent of which is obtained from the crude turpentine by distillation) amounted to 38,488,170 gallons in 1900, it had fallen to 30,687,051 in the year 1905, the number of installations then being 1287. The increased demand, coincident with decreased supplies, had raised the price considerably,[2] as will be gathered from the following tables giving the quantities and the value of the exported oil of turpentine.

Exports of Oil of Turpentine from the United States of America

	Gallons.
1901	20,240,851
1902	19,177,788
1903	16,378,787
1904	17,202,808
1905	15,894,813
1906	15,981,253
1907	15,854,676
1908	19,532,583
1909	17,502,028
1910	15,587,737
1911	14,817,751
1912	19,599,241
1913	21,039,597
1914	18,900,704
1915	9,464,120
1916	9,310,268
1917	8,841,875
1918	5,095,124
1919	10,672,102
1920	9,458,423
1921	9,267,959

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[1] *Journ. Ind. and Eng. Chem.*, 1915, 7, 837.

[2] Especially as the production of artificial camphor created a new demand.

Export of Oil of Turpentine from the United States of America

To	Value in Dollars.										
	1902.	1903.	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.	1912.
United Kingdom	3,419,764	3,553,172	4,438,779	3,849 060	4,091,643	3,822,156	3,744,459	2,858,449	3,133,732	4,209,265	3,977,620
Germany . .	1,101,175	1,009,808	1,402,982	1,261,633	1,624,066	1,884,384	1,874,547	1,213,703	1,495,019	1,283,741	1,387,677
Holland . .	950,784	920,567	782,884	984,181	1,082,722	1,207,652	1,330,329	1,010,249	1,266,990	1,117,875	1,673,650
Belgium . .	944,782	1,150,728	1,290,909	1,294,693	1,342,273	1,309,117	1,095,556	637,378	1,181,305	1,643,824	699,103
Italy . . .	146,687	251,573	177,420	114,303	184,233	148,371	244,557	89,807	116,659	56,972	127,542
Other countries .	868,056	1,128,474	1,353,181	1,398,231	1,752,331	1,870,407	1,856,703	1,208,472	1,586,531	2,456,525	2,203,443
Total . .	7,431,248	8,014,322	9,446,155	8,902,101	10,077,268	10,241,883	10,146,151	7,018,058	8,780,236	10,768,202	10,069,035

To	Value in Dollars.								
	1913.	1914.	1915.	1916.	1917.	1918.	1919.	1920.	1921.
United Kingdom .	3,057,468	2,930,570	2,416,284	2,415,677	2,473,266	659,989	5,995,538	7,153,298	2,699,643
Germany . .	1,515,468	1,368,616	90,313	...	...	...	17,125	113,251	...
Holland . .	1,718,862	1,870,304	293,127	207,448	35,078	...	585,380	718,372	529,977
Belgium . .	748,284	420,595	52,895	...	...	...	312,815	383,001	478,811
Italy . . .	70,320	14,725	84,109	46,853	77,511	160,225	490,731	12,895	13,591
Other countries .	1,684,254	1,491,148	1,539,578	1,667,585	1,727,815	1,875,721	3,046,645	6,202,485	2,309,990
Total . .	8,794,656	8,095,958	4,476,306	4,337,563	4,313,670	2,695,935	10,448,234	14,583,302	6,032,012

The American oil of turpentine is obtained from the turpentine of various species of *Pinus*, the most productive being *Pinus palustris*, the "long leaf" pine, and *P. heterophylla* (Cuban pine, slash pine), although also *Pinus tæda* (the Cuban "loblolly" or "rosemary" pine) and the "short leaf" pine are worked to advantage.[1] Similar in quality, though, as a rule, opposite in the sense of its optical rotation is the lævo-rotatory French oil of turpentine, which is obtained from the oleo-resin of *Pinus maritima* in the south and the south-west of France ("Landes"). The production of French oil of turpentine is very much smaller than that of American oil. Reliable statistical data as to the production are not available; it appears that most of the oil is consumed at home, the total export in 1904 amounting to 118,000 cwts., of which 9150 cwts. were sent to the United Kingdom. In the year 1905 the quantity exported to the United Kingdom had trebled, reaching 28,154 cwts. The following years show a gradually decreasing amount, being for the years 1908–13, 25,823, 20,390, 22,751, 23,635, 17,986, and 33,630 cwts. respectively; and in 1912–13 the exports from

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[1] The "pond pine" (*Pinus serotina*), which is found scattered among the forests of the "long leaf pine" along the Atlantic seaboard, yields an oleo-resin, the volatile oil of which was examined by Herty and Dickson (*Journ. Amer. Chem. Soc.*, 1908, 872). The oil had the specific gravity 0·8478 at 20° C., the iodine number 378; $[\alpha]^{20}_{D} = -105° \; 36'$, $n^{20}_{D} = 1{\cdot}4734$. One part of the oil required for solution at 22·5° C., 1·35 parts of 95 per cent, 4·80 parts of 90 per cent, 8·10 parts of 85 per cent, 16·20 parts of 80 per cent, and 56·00 parts of 70 per cent alcohol respectively. By fractionation the following results were obtained:—

°C.	Per cent.	$n^{20°}_{D}$.	Rotation in 100-mm. tube at 20° C.
172-175	27·4	1·4716	−87° 53′
175-180	57·0	1·4724	−92° 21′
180-185	8·4	1·4744	−92° 14′
Above 185	7·2	1·5045	..

Comparative evaporation tests with a volatile oil from the oleo-resin of *P. palustris* (*i.e.* the genuine American oil of turpentine of commerce) at the ordinary temperature, in shallow watch-glasses, using 0·2 grm., gave the following losses:—

Loss after	Oil from *P. palustris.*	Oil from *P. serotina.*
	Per cent.	Per cent.
½ hour	35·7	20·30
1 hour	62·5	37·30
1½ hours	91·7	53·40
2 hours	96·0	68·47
5 hours	97·8	98·8

With regard to the oxygen absorption power of the oil from *P. serotina*, it was found that during the first days it absorbed oxygen much more rapidly than did the oil from *P. palustris*, but the total absorption after three months' exposure was practically the same in each case.

The oil from this oleo-resin has not yet appeared in commerce, but as the oleo-resin will undoubtedly become admixed (in course of time) with the oleo-resin from *P. palustris*, attention should be paid to the fact that the boiling point of the oil, as obtained on an experimental scale by *Herty and Dickson*, is somewhat high. The characteristics of the oils obtained from the twigs and leaves of the Cuban pine (*Pinus heterophylla*) and the long leaf pine (*Pinus palustris*) are given by Schorger, *Journ. Ind. and Eng. Chem.*, 1914, 6, 723.

the United States to the United Kingdom were 7,865,713 and 6,432,271 gallons respectively.

Year.	Gallons.	Year.	Gallons.
1914	7,109,851	1918	1,413,732
1915	5,338,724	1919	6,220,048
1916	5,561,957	1920	5,238,621
1917	5,327,100	1921	4,423,954

The volatile oils contained in the oleo-resin yielded by species of pine indigenous to the Western States of America have been examined by *Schorger*,[1] with the following results :—

Source.	Yield from Oleo-Resin.	D_{15}.	N^{15}_{D}.	$[\alpha]_D$.
	Per cent.			Degrees.
Western yellow pine, *P. ponderosa*	18·5	0·8625	1·4772	−41·34
P. ponderosa scopulorum	19·6	0·8639	1·4723	+36·96
Lodgepole pine, *P. contaria*	14·7	0·8518	1·4860	−57·81
Pinon pine, *P. edulis*	20·0	0·8680	1·4707	+55·35

The American and French oils of turpentine, being obtained from the oleo-resin exuded by the **live** tree ("gum turpentine," "wood turpentine"), have a pleasant pine odour free from the empyreumatic smell which stamps the Russian oil (see below) as an oil of decidedly inferior quality.

Endeavours have been made to create an oil of turpentine industry in other countries. Thus the production of oil of turpentine from *Pinus halepensis* (cp. below) in Spain has been gradually increased during the last years, as will be seen from the following table, which shows the output of about twenty factories (which are under a trust : L' Union Resinera Española). The amount of "rosin" produced has also been added.

Year	Oil of Turpentine.	Rosin.
	Kilos.	Kilos.
1898–1899	1,866,821	6,534,661
1899–1900	2,336,288	8,375,535
1900–1901	2,379,301	8,167,005
1901–1902	2,287,671	7,972,650
1902–1903	2,549,309	8,706,474
1903–1904	3,146,896	10,825,256
1904–1905	3,440,815	12,090,555
1905–1906	3,589,324	12,157,241
1906–1907	4,330,699	14,601,375
1907–1908	4,610,735	15,350,547
1908–1909	4,684,712	15,766,465
1909–1910	4,652,594	15,369,629
1910–1911	4,727,873	15,235,741
1911–1912	4,477,355	16,214,797
1912–1913	4,971,161	16,820,258

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[1] *Eighth Int. Cong. Appl. Chem.*, 1912, sec. Ve, *Orig. Comm.*, xii. 181. For the examination of the oils distilled from the leaves and twigs cp. A. W. Schorger, *Journ. Ind. and Eng. Chem.*, 1915, 7, 24, and also M. Adams, *ibid.*, 1915, 7, 957.

Of the total output of Spanish oil of turpentine produced in 1912–1913, 77 per cent was exported, the remainder being consumed at home. The oil obtained by the steam distillation of the rosin from *Pinus halepensis*, largely grown in Andalusia, had the following characteristics[1] :—

Specific gravity at 20° C.	0·859
Optical rotation	–8·73
Refractive index	1·4654

Specimens of the oleo-resin from *Pinus halepensis*, which grows largely in Greece, Algiers, and France, yielded from 14·7 to 27 per cent of oil of turps. The specific gravity was 0·8552-0·8568, the specific rotation +46·6-47·6, and the refractive index at 25° C., 1·4638-1·4652. 80 per cent of these oils distilled over at 155°-156° C.[2] Oil of turpentine produced in Italy from *Pinus pinaster* yielded the following figures :—

Specific gravity at 15° C.	0·867-0·871
n_D^{20}	1·4700-1·4707
α_D	–35° at 26° C.
Flash point	33·5° C.

The oil began to distil at 154° C., 85-90 per cent coming over up to 163° C.[3]

The essential oil of *Pinus thumbergii*[4] grown in Japan has the following characteristics :—

Specific gravity at 15/4° C.	0·8740
n_D^{20}	1·4738
α_D	–19·17°

80 per cent of the oil distilled over between 154° and 169° C.

The imports into the United Kingdom from Spain and Portugal in the years 1908–13 were 6540, 1380, 6780, 5200, 6260, and 5900 cwts.

In India the production of (rosin and) oil of turpentine has been taken in hand under the auspices of the Government. The species *Pinus girardiana*, Wall. (North-West Himalayas and Garhwal), *Pinus Khasya*, Royle (Khasia mountains of Chittagong, Burma), *Pinus longifolia*, Roxb. (Himalayan slopes, North-West Kashmir), and *Pinus Merkusii* (Shan States, Martaban, Upper Tennasserim) seem to be suitable.[5] The oleo-resin from *Pinus longifolia* has been collected for distillation, especially during the last few years in the distilleries of Dehra, Dur-Nani-Tal, and Nurpur. The Government factories in Nurpur and Dehra are, however, closing down. In the year 1900–1901 over 22,000 trees were "tapped" and 1450 maunds[6] of turpentine were collected, which yielded 1600 gallons of oil of turpentine. In the year 1902–3, 43,000 trees were "tapped" and 3000 maunds[6] of oleo-resin distilled. In the year 1906 the production had been greatly extended, so that in the United Provinces about 11,664 gallons of oil were manufactured. In 1910 the productions had risen to 29,900 gallons, while in 1916, 31,445 gallons of turpentine were produced. It may be noted here that oil of turpentine as distilled in India contains a greater proportion of higher boiling fractions than do French and American oils.[1]

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[1] Obdulio, *Anal. Fis. Quim.*, 1909, 442.

[2] Vézes, *Chem. Zeit.*, 1912, 1189.

[3] M. Palazzo, *Annali Chim. Appl.*, 1917, 7, 88.

[4] Y. Shinosaki, *Journ. Chem. Ind.* Tokyo, 1918, 21, 763.

[5] The characteristics of the oil from *Boswellia serrata* are given in the *Bull. Imp. Inst.*, 1915, 13, 351.

[6] 1 maund = 82·3 lbs. (37·32 kg.).

According to private reports, the Mexican pine is also likely to yield (in the near future) considerable amounts of turpentine. The Mexican pine differs from the pine exploited in the United States in its habitat, the Mexican pine growing at an altitude of 5000-9000 feet, whereas the American pine grows at a height of 500 feet. The yield of turpentine per tree is stated to be much larger than that of the American pine. Reliable data are, however, not yet available. Up to the present the output of oil of turpentine and rosin appears to be very small. Considerable quantities of a volatile oil simulating ordinary oil of turpentine in its characteristics is obtained as a by-product in the manufacture of wood pulp.[2] The specific gravity of an oil so obtained is given by *H. W. Fosse* [3] as 0·8918, the major portion of the oil distilled between 157° and 160° C.

The greatest consumer of oil of turpentine is the United Kingdom, as will be gathered from the following table :—

Imports of Oil of Turpentine into the United Kingdom

Year.	Total Quantity.	Total Value.	From the United States.	
			Quantity.	Value.
	Cwts.	£	Cwts.	£
1901	643,846	842,742	618,972	819,327
1902	532,455	888,538	496,389	851,484
1903	533,109	1,028,934	460,324	938,184
1904	528,112	1,006,369	462,079	925,060
1905	526,679	1,104,300	424,892	972,693
1906	512,836	1,076,870	396,332	908,607
1907	510,308	975,166	389,828	814,532
1908	573,678	838,454	497,761	742,136
1909	443,375	699,807	365,967	612,324
1910	472,247	1,001,216	365,281	850,847
1911	480,130	914,028	363,485	739,027
1912	656,216	1,028,007	575,131	920,328
1913	560,330	768,800	476,400	670,549
1914	348,206	542,205	294,509	468,421
1915	529,517	903,381	418,050	727,574
1916	430,780	903,384	368,575	770,947
1917	221,192	620,747	202,633	565,055
1918	63,320	326,197	20,218	114,136
1919	455,839	1,940,001	381,132	1,591,953
1920	451,176	3,219,006	331,505	2,355,952

Accurate statistical data for Germany are not available, as oil of turpentine is classed together with pinolin, pine needle oil, rosin oil (and in the years 1905–9 also with camphor oil), as is stated in the following table :—

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[1] Puran Singh, *Indian Forest Records*, 1912, vol. iv. Part I.

[2] O. Halse and H. Dedichen, *Ber.*, 1917, 623.

[3] *Ber. Deutsch. Pharm. Ges.*, 1915, 25, 303.

	1905.		1906.		1907.		1908.		1909.	
	Import.	Export.	Import.	Export.	Import.	Export.	Import.	Export	Import.	Export.
Oil of turpentine, pine needle oil, rosin oil	Tons. 27,890 [1]	Tons. 1,700 [1]	Tons. 32,528 [1]	Tons. 1,462 [1]	Tons. 29,347 [1]	Tons. 1,271 [1]	Tons. 32,948 [1]	Tons. 1,414 [1]	Tons. 31,888 [1]	Tons. 1,245 [1]

	1910.		1911.		1912.		1913.		1920.	
	Import.	Export.	Import.	Export.	Import.	Export.	Import.	Export.	Import.	Export.
Oil of turpentine, pine needle oil, rosin oil	Tons. 28,282	Tons. 1,403	Tons. 27,326	Tons. 1,371	Tons. 30,455	Tons. 1,614	Tons. 35,024	Tons. 1,889	Tons. 4,089	Tons. 59

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[1] Includes camphor oil.

The following table gives the imports of rosin into the United Kingdom:—

	1910.	1911.	1912.	1913.	1914.
From—	Tons.	Tons.	Tons.	Tons.	Tons.
United States . . .	48,381	50,089	50,763	66,651	53,907
France	16,987	13,250	17,742	9,672	16,182
Spain and Portugal . .	8,160	8,644	10,091	8,350	6,224
All other countries . .	1,503	2,288	3,473	3,230	1,090

	1915.	1916.	1917.	1918.	1919.
From—	Tons.	Tons.	Tons.	Tons.	Tons.
United States . . .	52,931	75,745	65,114	18,275	57,240
France	37,856	14,580	14,864	15,806	21,366
Spain and Portugal . .	10,579	9,550	6,350	3,378	9,617
All other countries . .	1,047	215	...	162	798

From the above-given tables the quantities of oil of turpentine imported into Germany from the United States can be computed. In the difference there would be included the import of Spanish oil of turpentine, and most notably the Russian and Finnish oils of turpentine.

Genuine oil of turpentine ("Gum Turpentine oil," "Box[1] Turpentine oil") should have a specific gravity of 0·865 at 15·5° C., should yield on fractionation (determination of the boiling point) 90 per cent of distillate from 155° to 165° C., should have a flash point of about 92°-94° F.[2] in *Gray's* apparatus, absorb about 400 per cent of iodine,[3] and have a refractive index of 1·47 at 20° C.[4] In the following table (see p. 174) the analytical data of two different specimens of genuine American oils of turpentine are given. With regard to the iodine test some details are added which show that on using an excess of iodine of 110-135 per cent the highest results are obtained after sixteen hours' standing.

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[1] H. Wolff, *Chem. Zeit.*, 1912, 762, so called from the process of collecting the turpentine in boxes.

[2] The flash point of a sample of Finnish turpentine examined by Nash (*Analyst*, 1911, 577) was 67° F.

[3] The determination of the bromine absorption (Vaubel, *Pharm. Zeitung*, 1906 (51), 257) in place of the iodine test cannot be recommended (cp. Vol. I. Chap. X.).

[4] The generally accepted opinion that American oil of turpentine is dextro-rotatory has not been borne out by examinations. Herty (*Journ. Amer. Chem. Soc.*, 1908, 863) states that whilst oil obtained from turpentine at different times of the year from one and the same tree remains fairly constant in its optical rotation, oils obtained from oleo-resins from different trees of the same species and growing quite close to each other exhibit wide variations. Thus oils from *P. palustris* exhibited rotations from +1° 23′ to +18° 18′ in a 100-mm. tube at 20° C., and oils from the turpentine from *Pinus heterophylla* rotations ranging from +0° 15′ to −29° 26′. These observations explain satisfactorily the apparently conflicting statements occurring in the literature on this subject (Valenta, *Chem. Zeit.*, 1905, 807). The oil from *Pinus halepensis* had the rotation +47° and the oil from the buds of the same tree had +39·4°, whereas *Pinus maritima* had −40·5° (D. E. Tsakalotos, *Gaz. Chim. Ital.*, 1917, 47, I. 285). With regard to the rotatory dispersion of oil of turpentine, see E. Darmois, *Compt. rend.*, 1908 (147), 195.

It should be noted that, in contradistinction to "wood (oils of) turpentine" (see below), the several fractions obtained in the boiling point test give approximately the same numbers, a fact which is of importance in the examination of substitutes and adulterated specimens.

The part which oil of turpentine plays in the process of "drying" will be discussed below, p. 191.

Of distinctly inferior quality to the American and French oils of turpentine is the *Russian oil of turpentine*, and its substitution for American and French oil of turpentine without a specific declaration as to its origin is not admissible.

This oil is obtained by distillation of the (dead) waste wood and roots[1] of the Scotch fir (*Pinus sylvestris*), and is best known under its German name "Kienöl" ("Pine Oil"). The oil has an unpleasant empyreumatic odour, which a varnish prepared with it will give off whilst drying. Hence this oil is entirely unsuitable for varnishes used for indoor work. This serious drawback has led to the designing of processes for the deodorisation of the Russian oil, such as distilling over lime or caustic soda, metallic sodium, metallic calcium,[2] or treatment with ammonia under pressure[3] or with oxidising agents (permanganate,[4] chromic acid, persulphates, ozone) followed by distillation over lime[5] or zinc dust.[6]

For the detection of small quantities of pine oil in oil of turpentine *Piest*[7] gives the following test:—5 c.c. are shaken with an equal volume of acetic anhydride and 10 drops of hydrochloric acid. The mixture is cooled and shaken after the addition of a further 5 drops of hydrochloric acid. After cooling the solution has a faint yellow colour if the oil of turpentine be pure, whereas if pine oil is present, darkening of the solution takes place.

It may be added here that *Schindelmeiser* isolated from "Kienöl" the following substances: toluene, cymene, a quinone-like substance having a pungent smell, nopinene, sylvestrene, dipentene, and hydrocarbons of the methane series. From the highest boiling fraction of "Kienöl" there was obtained a sesquiterpene identical with an optically inactive hydrocarbon which is associated with cadinene in oil of cade.

The products now placed on the market are of much superior quality to those that were delivered some six or eight years ago, but they cannot rank on a par with American or French oil.

The Russian oil is chemically differentiated by a much lower iodine value, lower specific gravity, and higher boiling point. Russian oil contains only a small quantity of pinene.[8]

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[1] Hence this oil is also known as "Wurzelstocköl."

[2] Cp. A. Hesse, English patent 7934, 1906; German patent 180,499; United States patent 835,907. Cp. also Sprenger, Belgian patent 210,591.

[3] J. Schindelmeiser, German patents 239,546, 253,241.

[4] Tassilly and Sterkers, French patent 441,501.

[5] E. Heber, English patent 10,004, 1903; United States patent 830,069, 1906; Carl Kaas, German patents 170,543, 180,207; O. P. Pellnitz, German patents 202,254, 218,337; United States patent 910,146; Hecker and Zeidler, German patent 196,907.

[6] L. Ahlers, German patent 204,391.

[7] *Chem. Zeit.*, 1912, 198.

[8] Henderson and W. J. S. Eastburn, *Journ. Chem. Soc.*, 1909, 1466.

A sample of "virgin" Russian turpentine examined by *Parry*[1] gave the following figures:—

	Crude.	Rectified.
Specific gravity at 15° C.	0·867	0·8646
Rotation	+7° 50′	+8°
Refractive Index	1·4718	1·4890
Distillation test:—		
Below 155° C.	Traces	Nil
155°-160° C.	65 per cent	68 per cent
160°-165° C.	11 ,,	13 ,,
165°-170° C.	13 ,,	10 ,,
170°-180° C.	7·5	7
Over 180° C.	3·5	2

The analysis of an oil of this type is given under No. 3 of the following table, p. 174. Such an oil is easily recognised as a Russian oil by its unpleasant (empyreumatic) smell, which becomes distinctly noticeable if a few drops are poured on to a strip of filter-paper and allowed to evaporate slowly. It is further recognised as a "wood oil" by the sulphurous acid test (*Conradson*).[2] On shaking equal quantities of oil and sulphurous acid of specific gravity 1·030, the oil, which separates on the top, has a dark yellow colour. Mixtures of this oil with genuine oil of turpentine are in this test readily recognised by a green coloration of the oil. If the percentage of Russian oil in a genuine oil of turpentine is small, the sulphurous acid test leaves room for doubt. Reliance must then be placed on the smell of the sample, which should be allowed to evaporate slowly by exposure to the atmosphere.

The quantity of Russian oil of turpentine exported to the United Kingdom is given in the following table:—

Russian Oil of Turpentine imported into the United Kingdom

Year.	Quantity.	Value.
	Cwts.	£
1901	21,956	19,882
1902	27,875	24,249
1903	56,304	60,155
1904	52,709	58,147
1905	68,754	67,117
1906	78,334	91,956
1907	95,422	110,271
1908	35,885	34,938
1909	51,617	49,848
1910	70,707	75,108
1911	78,245	95,707
1912	48,713	58,332

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[1] *Chemist and Druggist*, 1912, 75.

[2] *Journ. Soc. Chem. Ind.*, 1897, 519. In the continental literature this test is described as the *Herzfeld* test, although Herzfeld's first publication appeared in *Zeits. öffentl. Chem.*, 1904, 382. It may be added that Herzfeld still claims (*Chem. Revue*, 1908, 11) the sulphurous acid test as having been suggested by him.

During recent years Russian oil has also been imported in the United States, where it is no doubt used to adulterate genuine American oil.

Finnish (Swedish) oil of turpentine from wood, as also "pine needle oil," obtained by distilling the fir needles,[1] and the so-called "Sulfat turpentine oil,"[2] have a similar character, and can at best only be considered as inferior substitutes of the genuine oil of turpentine.[3] The Finnish oils are dextro-rotatory.

The scarcity of genuine oil of turpentine in America (in 1907–8) has led there also to the distillation of branches and roots of the pine tree (dead wood), and thus an oil was produced which was at first sold under special names, such as "wood oil," "pine knot oil," "wood turpentine," "pine wood turpentine." Its empyreumatic odour, similar to that of the Russian oil, and its inferiority as regards imparting drying power to a varnish, readily characterised this product as a low-grade oil. Thus an oil obtained by dry distillation of dead wood gave an oil having the specific gravity 0·9231 at 15° C. and of a very dark colour. During recent years a considerable improvement of the product has been effected by careful distillation of the wood in a current of steam,[4] followed by careful fractionation and chemical purification. An oil so obtained had the specific gravity 0·8834 at 15° C. and the refractive index 1·4749 at 15° C.[5] A product of the same origin but after being refined, had the specific gravity 0·8698 at 15° C. and the refractive index 1·4709 at 15° C. Thus, whereas several years ago such oils were readily recognised by low iodine values—about 212[6] for "refined wood turpentine" and 328 for "water white" quality—a commercial specimen which the author examined—No. 4 of the table, p. 175, closely approaches the iodine absorption of genuine oil. It will be further seen from the numbers given in the following table for 4*a* and 4*b* that by further fractionation of this sample the first 84 per cent reached almost the normal iodine value of genuine oil of turpentine.

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[1] Cp. J. J. Kondakow and J. Schindelmeiser, *Chem. Zeit.*, 1906, 722; O. Aschan, *Zeits. f. angew. Chem.*, 1907, 1811. Cp. also *ibid.*, 1908, 468; Bergström and Fagerlind, *Chem. Zeit. Rep.*, 1908, 641.

[2] This is a low-class oil of turpentine recovered as a by-product in the manufacture of cellulose by the sulphate process (Vilarson and Person, *Journ. Soc. Chem. Ind.*, 1907, 278). It contains as impurities organic sulphides which can be removed by treatment with sulphuric acid containing 50 per cent monohydrate, and subsequent distillation in a current of steam. Klason, *Papier Zeit.*, 1908, 3779; cp. Bergström, *Chem. Zeit. Rep.*, 1909, 35. Cp. also O. M. Halse and H. Dedichen, *Ber.*, 1917, 50, 623.

[3] For a process of deodorising "sulfat turpentine oil" by means of nitrous oxides, see German patent 210,829 (C. G. Schwalbe).

[4] From the large number of patents, most of them repetitions of earlier patents, the latest may be selected:—J. G. Gardner, United States patent 808,035; G. O. Gilmer, United States patent 813,088; F. S. Davis and Richardson, United States patent 826,407; F. M. Gideon, United States patent 832,311; J. G. Saunders, United States patent 834,759; Hale and Kürsteiner, United States patent 828,474; J. T. Denny, United States patent 834,875; G. R. Pride, United States patent 840,955; M. M'Kenzie, French patent 367,926; United States patents 851,687, 852,236; German patent 200,157; K. Bosch, French patent 357,391; F. T. Snyder, French patent 368,198; English patent 19,870, 1906; United States patent 821,264; H. Rasche, United States patent 850,098; F. Pope, United States patent 852,078; J. W. Thompson Raleigh and Newsom, United States patent 862,680. A criticism of these processes is given by Teeple, *Journ. Soc. Chem. Ind.*, 1907, 812. Cp. also J. Walker, United States patent 922,369.

[5] United States Dept. of Agricult. Forest Service; cp. *Chem. Zeit.*, 1909, 859.

[6] Worstall, *Journ. Soc. Chem. Ind.*, 1904, 301.

These highly refined wood turpentine oils approach in their boiling points and iodine values so closely to the genuine oils that they can be differentiated from the latter only by the sulphurous acid test and by their smell. For mixtures of 20-30 per cent of "wood oil" with 80-70 per cent of genuine oil the sulphurous acid test is of doubtful value, and fails completely if the percentage of "wood oil" falls still lower.

In such cases—which, however, hardly occur in practice, as the cost of refining renders the admixture of so small an amount unremunerative—the smell of the sample itself or of the residue from a distillation will serve as a guide. Confirmation of a suspicion can then be obtained by the chemical examination of the several fractions, into which the oil is resolved by distillation (cp. Nos. 4*a* and 4*b* of the following table). *Hawley*[1] states that wood turpentines contain large amounts of dipentene and heavy oils, their proportion depending to a great extent on the temperature employed in the distillation of the crude wood turpentine.

To the class of wood oils belongs the "long leaf pine oil," the oil which is obtained as a by-product in the extraction of turpentine from "lightwood"[2] (*i.e.* from portions of the tree which have been cut at least three years and are very resinous) by means of steam. This oil, which now comes into the market in considerable quantities, has a specific gravity ranging from 0·935 to 0·947, begins to distil at about 206°-210° C., and yields 75 per cent between 211°-218° C., or 50 per cent between 213° and 217° C. A sample of the specific gravity 0·945 at 15·5° C. had the specific rotation $[\alpha]_D^{20} = -11°$, and the refractive index $n_D = 1{\cdot}4830$.[3] The oil consists essentially of terpineol, $C_{10}H_{18}O$,[4] and gives, by treatment with 5 per cent of sulphuric acid, terpene hydrate, $C_{10}H_{20}O_2 + H_2O$, with a yield of 60 per cent of the theoretical one. According to *Teeple*, the formation of terpineol appears to be due to the gradual absorption of 1 molecule of water by the pinene of the oleo-resin, after the death of the tree.[5] The long leaf pine oil is stated to dissolve any of the ordinary gum-resins without it being necessary to subject them to the heating process.

In the chemical examination of oil of turps, *Nicolardon and Clément*[6] recommend to fractionate under pressure of 18 cm. of mercury, the distillation being complete at 50° C. The presence of rosin oil is shown by an increasing amount of the residue left after distillation.

Whereas the best refined "wood oils" may serve as substitutes for genuine oil of turpentine if sold under their proper name, the numerous "substitutes," mostly sold under fancy names, must be regarded as adulterated oils. The analysis of two such oils is given in the following table under No. 5 and No. 6.

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[1] *VIII. Int. Congr. Appl. Chem.*, 1912, Sect. Ve, 41.

[2] Teeple, *Journ. Soc. Chem. Ind.*, 1907, 811.

[3] Teeple, *Journ. Amer. Chem. Soc.*, 1908, 412.

[4] Walker, *Bull. Mass. Inst. of Tech.*, 1905, September.

[5] With regard to the chemistry of the hydrocarbons in oil of turpentine, cp. also C. B. Frankforter and F. C. Frary, *Journ. Amer. Chem. Soc.*, 1906, 1461.

[6] *Compt. rend.*, 1909 (149), 572.

It will be seen that the last sample, No. 6, contains much more of the adulterant than does No. 5. The usual adulterants of turpentine oil are rosin spirit (pinolin [1]), rosin oil,[2] and especially petroleum hydrocarbons of the same boiling point.[3] All these are easily detected by the determination of the specific gravity, boiling point, iodine value, and refraction of the sample or (and) of its fractions; thus the amount of adulterant can be derived with sufficient accuracy for practical purposes.[4] The iodine values of rosin spirit and rosin oil are about 180 and 100 respectively; the iodine value of petroleum hydrocarbons [5] is very low or *nil*. *Grimaldi and Prussia* [6] base a method for the determination of petroleum hydrocarbons on the oxidation of the oil by mercuric acetate and the solubility of the resulting product in dilute nitric acid. The method is carried out as follows:—75 grms. of mercuric acetate are placed in a graduated flask of 500 c.c. capacity, having also a graduation on the neck from 0 to 10 c.c. The mercuric acetate is dissolved in 200 c.c. of water, 100 c.c. of glacial acetic acid and 10 c.c. of the oil are added and the flask heated for two hours at 80° C. under a reflux condenser with constant shaking. After cooling, the flask is filled up to the mark with nitric acid (2 parts of nitric acid of specific gravity 1·4 and one part of water) and shaken. After settling, the volume of insoluble oil is read off. There is, however, a loss of from 0·35 to 0·7 c.c. in the volume of the insoluble hydrocarbons. Proposals by *Tausz* [7] to determine volumetrically the acetic acid formed in the reaction or alternatively to weigh the reduced mercurous salt formed have been condemned by *Salvaterra*.[1] For the somewhat debatable methods proposed by *Salvaterra* for the determination of wood turpentine the original paper must be consulted.[1] *Nash*[2] gives as a rapid test the shaking up of a measured volume in a graduated tube and comparing the amount of froth with that produced by mixtures of known composition: turpentine alone gives no froth. *Richardson and Whitaker*[3] propose a method for the determination of benzol and its homologues, based on the conversion of these aromatic hydrocarbons into sulphonic acids by treatment with fuming sulphuric acid; the excess of sulphuric acid is neutralised with barium carbonate, the barium sulphate filtered off and the barium present in the solution as barium sulphonate is determined in the usual manner. *V. E. Grotlisch and W. C. Smith*[4] separate the turpentine as pinene hydrochloride by saturating the oil with dry hydrochloric acid gas in the cold, and subsequently distilling the mixture under reduced pressure before the sulphonation is carried out.

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[1] Grimaldi (*Chem. Zeit.*, 1907, 1145; *Atti del VI. Congresso di Chimica Applicata*, Rome, vol. v. 365) proposes the following colour reaction as characteristic of pinolin: (1) An emerald-green coloration with tin and concentrated hydrochloric acid. 100 grms. of oil are distilled fractionally, and the first 5 fractions of 3 c.c. each, as also the following fractions, taken in intervals of 5° C. up to 170° C., are tested with hydrochloric acid and tin, the test-tube being kept in a boiling water-bath. In the case of pure pinolin a deep emerald-green coloration is observed. The presence of 5 per cent of pinolin in oil of turps, or of 10 per cent "Kienöl," can be detected. If the colour reaction be indistinct, the experiment should be repeated with 200-400 grms. of substance. (2) A yellow coloration changing to green with bromine vapours. The fractions are prepared as described under (1). One drop is placed in a porcelain dish, and 2 c.c. of a reagent, prepared from 1 volume of crystallised carbolic acid and 2 volumes of carbon tetrachloride, are added and vapours of a solution of bromine in carbon tetrachloride blown over it.

[2] A colourless rosin oil of less than 0·9 specific gravity and boiling point about 130°-200° C. is frequently used for adulteration.

[3] Coste and Nash, *Analyst*, 1911, 207.

[4] For the determination of petroleum hydrocarbons by means of concentrated sulphuric acid (proposed by Armstrong, *Pharm. Journ.*, 1882, 584), cp. J. M. M'Candless, *Journ. Amer. Chem. Soc.*, 1904, 26; Böhme, *Chem. Zeit.*, 1906, 633; R. Adan, *Bull. Soc. Chim. Belg.*, 1908, 389; Morrell, *Journ. Soc. Chem. Ind.*, 1910, 241. Cp. A. Kreiger, *Chem. Zeit.*, 1916, 40, 472; *Report of the American Society for Testing Materials*, 1914, 91; also *U.S. Dept. Agric. Bureau Chem. Bull.*, 898, 43. For Burton's nitric acid test, proposed in 1890, see *Journ. Soc. Chem. Ind.*, 1910, 241, and Marcusson, *Chem. Zeit.*, 1909, 979, 985.

[5] For the rapid detection and determination of petroleum naphtha in turpentine H. C. Frey (*Journ. Amer. Chem. Soc.*, 1908, 420) recommends to measure 10 c.c. of a suspected sample into a 50-c.c. stoppered measuring cylinder, to add 30 c.c. of aniline, and shake violently for five minutes. If any petroleum naphtha is in the sample, it will float on the top and its volume can be read off. Frey states that this method gives very good results if care be taken that the aniline is free from water.

[6] *Ann. Chim. Appl.*, 1914, 324.

[7] *Chem. Zeit.*, 1918, 42, 349.

Rosin spirit gives a green coloration with sulphurous acid. *Veitch and Donk*[5] state that if rosin spirit is present treatment with sulphurous acid produces a red coloration; a green colour being given by hydrochloric acid. Recently carbon tetrachloride has been used for adulteration, chiefly to mask the presence of petroleum hydrocarbons, which lower the specific gravity (see No. 6 of the following table). Several patentees claim the addition of carbon tetrachloride to oil of turpentine on the plea that it renders the latter non-inflammable.[6] This statement is, however, not borne out by facts, and it would rather appear that the carbon tetrachloride is added to "correct" the low specific gravity of added petroleum hydrocarbons. The detection of carbon tetrachloride offers no difficulty. Oil of turps to which copal oil has been added exhibits inferior drying powers to the pure oil, inasmuch as the residue left on drying has an oily consistence and a strong acid reaction. It is also said to produce inflammation when brought into contact with the skin.[7] In the preparation of turpentine substitutes from petroleum hydrocarbons those fractions are taken which distil between 70° and 120° C., and are deodorised by treatment with sulphuric acid, followed by a solution of bisulphite and finally with alkaline water. After drying, the product is mixed with natural turpentine with the addition of small amounts of camphor, rosin, and terpene in order to raise the gravity of the mixture.[8]

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[1] *Chem. Zeit.*, 1921, 45, 133, 150, 158.

[2] *Analyst*, 1909, 151.

[3] *Journ. Soc. Chem. Ind.*, 1911, 115.

[4] *Journ. Ind. Eng. Chem.*, 1921, 13.

[5] *Bull. United States Dept. Agric.*, 1911 (135), 29.

[6] English patent 21,954 (G. H. Harrison); A. Pollet, French patent 354,425, and First Addition No. 6170.

[7] Vaubel, *Zeits. f. angew. Chem.*, 1910, 1165.

[8] Valette, French patent 415,218.

[TABLE

Analyses of Genuine Oils of Turpentine, Russian Oil of Turpentine, Wood Oil, and Adulterated Oils (Lewkowitsch)[1]

	Specific Gravity.	Boiling Point.		Flash Point in Gray's Tester.	Iodine Test (Wijs' Method).			
		° C.	Yield.		Excess of Iodine. Per cent.	Time allowed to stand. 20 min.	4 hrs.	16 hrs.
No. 1 Genuine oil Gum Turps	0·8685	156-157	38%	93° F.	118	...	379·6	...
		158	62%		181	388·2	...	...
		159	84%		109	...	...	402·0
		160	92%					
No. 2 Genuine oil Gum Turps	0·8686	154-155	7%	94° F.	75	...	317·5	...
		157	45%		145	...	390·0	...
		159	84%		147	380·4	...	...
		160	95%		135	...	...	403·5
No. 3 Russian oil	0·8610	160-161	5%	...	240	298·2	...	...
		163	12%		157	...	...	317·0
		165	24%		175	...	311	
		169	50%					
		170	57%					
		175	76%					
		178	82%					
		180	85%					
		185	90%					
3*a* Distillate 50 per cent .	0·8562							
3*b* Distillate next 40 per cent .	0·8601							
3*c* Residue 10 per cent .	0·9022							

The author can confirm (from his own examination) the reliability of this test for approximate quantitative determination.

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[1] Cp. also F. W. Richardson and Bowen, *Journ. Soc. Chem. Ind.*, 1908, 613, and J. H. Coste, *Analyst*, 1908, 219; 1909, 150; 1910, 112. Criticism by Coste of Richardson and Bowen's method, see *Analyst*, 1910, 113.

Analyses of Genuine Oils of Turpentine, Russian Oil of Turpentine, Wood Oil, and Adulterated Oils (Lewkowitsch)—continued

		Specific Gravity.	Boiling Point.		Flash Point in Gray's Tester.	Iodine Test (Wijs' Method).			
			°C.	Yield.		Excess of Iodine.	Time allowed to stand.		
							20 min.	4 hrs.	16 hrs.
No. 4	"Wood oil," refined .	0·8677	155-156	2%	95° F.	Per cent. 163	...	377·7	...
			157	12%		121	...		380·9
			158	28%					
			159	40%					
			160	50%					
			161	60%					
			162	66%					
			163	70%					
			164	76%					
			165	78%					
			166	80%					
			170	84%					
4*a*	Distillate 84 per cent .					151	...	389·5	...
4*b*	Residue 16 per cent .					211	...	291·2	...
No. 5	Oil of turps substitute .	0·8472	147-150	1%	93° F.	271	...	233·4	...
			155	9%					
			156	14%					
			157	18%					
			160	28%					
			162	36%					
			165	44%					
			170	56%					
			175	64%					
			180	68%					
			185	72%					
			190	75%					
			195	77%					
			200	80%					
			205	82%					
No. 6	Oil of turps substitute .	0·8203	145-150	3%	94° F.	1377	...	78·86	...
			155	5%					
			160	10%					
			165	15%					
			170	20%					
			175	27%					
			180	32%					
			185	38%					
			190	43%					
			195	49%					
			200	54%					

The function of the oil of turpentine in a varnish is to act as an oxygen (and (or) ozone) carrier, thus assisting the drying of the gum-resin and of the drying oil (cp. p. 191). It is very likely that if ozone be formed, the latter would exercise a bleaching effect as well. When the varnish dries, part of the oil of turpentine becomes resinified and assists in furnishing a more elastic coat than would be obtained without the oil of turpentine. Rosin spirit and rosin oil leave a sticky residue behind, which greatly retards the drying of the oil and gum-resin (most likely by preventing the free access of air). The petroleum hydrocarbons volatilise completely, but fail to impart any drying properties.

Non-volatile Portion of the Varnish

The residue left in the flask after the removal of the volatile portion is freed from water. By ascertaining the amount of glycerol it yields on saponification, the proportion of " boiled oil " can be approximately arrived at. *M. Seaton and G. Sawyer*[1] state that the fatty constituents of a varnish can be detected by the freezing point method, using stearic acid as a solvent. In the case of varnishes prepared from polymerised tung oil and colophony, *E. Ware and C. L. Schumann*[2] state that an approximate separation can be obtained by treating the sodium salts of the fatty acids with absolute alcohol in which the rosin soap is very soluble. The separation of the gums from the boiled oil cannot always be carried out satisfactorily in the manner in which rosin acids are separated from fatty acids (see Vol. I. Chap. X.), as many of the gum-resins are incompletely soluble in absolute alcohol, and others which are soluble give a heavy precipitate on treatment with hydrochloric acid gas. Hence an attempt made by the author to differentiate between gum-resins and colophony (which is used as an adulterant in cheap varnishes) ended in failure, as some of the results reproduced in the following table indicate[3] :—

	Soluble in Absolute Alcohol.	Gum-Resin recovered by Twitchell's Process.
	Per cent.	Per cent.
Copal I. . . .	93	84
,, II. . . .	55	29·9
Mastic	84·4	35·5

The characteristics of gum-resins—such as acid value, saponification value, etc.—do not lead to decisive information, for it must be borne in mind that the gums are heated to about 300° C., so that their chemical composition becomes entirely changed. *Lewkowitsch*[1] examined a number of gum-resins used in the manufacture of varnishes both in their original state and after heating to 300° C. The numbers, given in the following table, may serve as a guide in the analysis of varnishes :—

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[1] *Journ. Ind. and Eng. Chem.*, 1916, 8, 490.

[2] *Journ. Ind. and Eng. Chem.*, 1915, 7, 571.

[3] W. Fahrion, *Chem. Revue*, 1913, 177, and H. Wolff and E. Svholze, *Chem. Zeit.*, 1914, 38, 369, 382. Cp. also H. Smit-Addens, *Zeits. f. angew. Chem.*, 1918, 31, 142.

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[1] *Analyst*, 1901, 37 ; cp. also Worstall, *Journ. Amer. Chem. Soc.*, 1903, 860 ; Coffignier, *Bull. Soc. Chim.*, 1906 (35), 762.

[Table

Some Characteristics and Variables of Gum-Resins used in Varnishes (Lewkowitsch)

	Original Gum-Resins.						Gum-Resins after Heating to 300° C.				
	Acid Value.	Saponification Value.	Unsaponifiable. Per cent.	Iodine Value.		Soluble in Alcohol. Per cent.	Acid Value.	Saponification Value.	Unsaponifiable. Per cent.	Iodine Value.	
				By ICl. addition.	By Bromine addition.					By ICl. addition.	By Bromine addition.
Copal, Commercial	109·8	143·1	7·96	135·5	183·6	93·06	26·49	85·4	14·73	124·3	181·3
Copal, Commercial	42·43	66·82	14·99	191·2	114·6	54·83	24·94	61·04	46·40	143·7	233·5
Copal, Sierra Leone	72·83	119·03	18·81	105·7	96·05	...	12·89	114·9	17·22	125·5	173·6
Copal, Manila	127·6	175·17	15·98	137·9	188·2	...	68·21	136·3	22·99	133·3	186·4
Copal, Brazil	108·99	171·4	7·66	127·7	72·66	...	46·25	113·8	38·74	136·7	225·9
Copal, Sierra Leone	65·7	110·5	16·27	94·55	117·0	...	15·32	123·8	22·31	95·23	135·4
Kauri	37·39	53·84	20·07	90·99	...	...	17·14	61·07	10·39	67·70	74·71
Mastic	52·73	81·79	51·13	175·7	185·0	84·41	23·23	50·24	49·28	165·0	217·8
Shellac, Dark	61·13	203·0	3·56	35·57	13·25						
Sandarac, Mogador	134·39	143·42	13·2	112·2	99·98	...	64·84	136·14	14·28	126·4	69·13
Sandarac, Australia	131·15	134·32	17·44	125·4	63·83	...	106·6	137·26	9·93		
Animi No. 1	18·69	73·15	6·3[illegible]	105·3	182·7	...	9·25	58·73	...	106·1	207·4
Animi No. 2	30·22	93·5	6·85	96·21	95·85						
Dammar	35·22	32·73	75·96	127·5	169·4	...	10·85	60·44	86·57	127·0	196·8
Amber	16·7	121·27	18·86	58·98	82·82						
Succinit	11·24	113·68	7·06	55·05	78·4	...	10·60	99·19	16·25	74·34	147·8
Colophony	...	...	...	...	...	...	146·46	153·01	15·94	133·7	302·1

Stewart[1] states that dammar may be detected in kauri by first extracting the gum with alcohol following the extraction of the insoluble residue with chloroform. He states that kauri gives no matter which is insoluble in alcohol and soluble in chloroform, whereas in the sample of dammar he examined the chloroform extract amounted to 36·4 per cent. Too much reliance must not, however, be placed on this for, as *Parry*[2] shows, the statement is only true for the finest and whitest quality of kauri, the darker-coloured samples giving totally different solubilities.

The following table due to *Puran Singh*[3] is reproduced here :—

	Moisture (expelled at 100° C.).	Matter insoluble in hot Alcohol.	Acid number (A).	Saponification number (B).	Iodine absorption (Hübl) after 18 Hours' Action.
	Per cent.	Per cent.			Per cent.
Shellac from Kusum lac	2·7	0·7	61·1	201·0	9·6
Shellac from Palaslac .	3·8	0·8	60·8	202·4	9·3
Shellac from Block lac .	3·9	1·1	63·1	201·6	8·2
Mirzapur Factory Shellac	2·0	0·6	64·4	203·6	8·6
Lac wax (m.p. 58°-59° C.	...	...	22·1-24·3	79·2-85·0	8·8
Lac resin (desiccator dry)	...	...	52·1-59·2	193·5-198·4	6·8-7·3
Lac resin (melted) . .	...	...	54·9	190·0	5·9

McIlhiney separates the products obtained after saponification of the non-volatile portion of the varnish into three fractions. (1) " Hard gum " insoluble in petroleum ether and in dilute alcohol, (2) fatty acid soluble in petroleum ether (this fraction will contain any rosin acids which may have been added in the form of colophony), and (3) an aqueous layer containing the glycerin resulting from the saponification of the oil. It must, however, be borne in mind that this method can only lead to approximate results, for, in the first instance, the oxidised acids formed during the boiling of the oil will remain in the fraction insoluble in petroleum ether, *i.e.* in the " hard gum." Errors will also be due to the different behaviour of the great variety of gums used for varnish making. The properties of these gums are too little known to allow of any great reliance being placed on methods based on the solubilities in various solvents. The method, however, will furnish some assistance in the examination of varnishes.

McIlhiney[4] operates as follows :—2-10 grms. of substance are saponified with a measured quantity of half normal caustic potash. The major portion of the solvent is then distilled off and the residue dissolved in neutral absolute alcohol. By titrating back with a standard solution of acetic acid in absolute alcohol, the saponification value is found. The fatty and rosin acids are liberated by the addition of the exact amount of alcoholic acetic acid, and an amount of petroleum ether is added sufficient to dissolve the fatty acids. Water is now added carefully until separation occurs; the petroleum ether layer is poured off, washed with water and distilled. The residue after weighing may be resolved into fatty and rosin acids by the method given in Chap. VIII. The residue "gard gum" is washed with petroleum ether and dilute alcohol and weighed. It may be possible to separate this or to remove the oxidised acids by means of 85 per cent alcohol. For a method of differentiating copals from various sources by their solubility in chlorinated hydrocarbons, see *C. Coffignier.*[1]

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[1] *Journ. Soc. Chem. Ind.*, 1909, 350.

[2] *Oil and Colour Trades Journ.*, 1909, 1765.

[3] *Journ. Soc. Chem. Ind.*, 1910, 1435; cp. also Wolff, *Chem. Revue*, 1914, 159.

[4] *Proc. Amer. Chem. Soc.*, 1908, vol. viii. 596.

The amount of oxygen absorbed by the different gum-resins appears to be approximately the same. This may be gathered from the numbers given in the following table :—

Oxygen Absorptions of Varnish Oils (Lewkowitsch)

Varnish Oil prepared from	Increase in weight of the Varnish Oils kept under a bell jar, protected from dust, but with free access of air.	
	After days.	Per cent.
Sandarac	352	7·56
Mogador	352	7·68
Copal No. 1	351	6·71
Copal No. 2	347	6·57
W. G. Rosin	351	7·37
Mastic	347	6·77
Animi	347	8·19
Cowrie	346	6·75
Sandarac, Australian	346	7·87
Amber	338	7·08

It should, however, be pointed out that these numbers must be used with the greatest circumspection.

The detection of colophony, which in highly priced varnishes must be looked upon as an adulterant, is not always possible by chemical means; at any rate its quantitative determination, if it be present in admixture with gum-resins, must be considered as impossible in the present state of our knowledge.[2] The indications furnished by the colour reactions obtained with *Halphen's* reagent[3] must be accepted with reserve.

A series of practical examinations (by *Weger*) of a number of boiled oils, varnish oils, and rosin oils, as regards their drying power, is given in Table No. 38 of the *Laboratory Companion to Fats and Oils Industries.*

The examination of *the ash* will indicate what metal or metals have been used as driers. Considerable quantities of lime in the ash point to the addition of calcium rosinate (German—*Harzkalk*) which is frequently used in excessive quantities to give the dried coat of varnish a fictitious hardness and gloss. This gloss disappears somewhat rapidly on exposure to moisture, with formation of white spots, caused by the decomposition of the rosinate into rosin acid and lime.[1] The chemical examination must be supplemented by practical tests.

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[1] *Bull. Soc. Chem.*, 1914, 15, 780.

[2] The method suggested by A. H. Gill (*Journ. Amer. Chem. Soc.*, 1906, 1723) must be accepted with the greatest reserve. Cp. McIlhinev *Chem. Engineer*, 1908, 70.

[3] Hicks, *Journ. Ind. Eng. Chem.*, 1911, 86.

The most useful results are obtained by painting the varnish on the special material (wood, iron) on which it is to be applied ultimately.

Physical tests are of minor importance. The determination of the viscosity of varnishes has been proposed by *Valenta*. *Laurie and Baily* [2] suggest the determination of the hardness by means of a special apparatus,[3] in which a smooth hard plate, coated with the varnish to be tested, is drawn across a polished blunt point which is pressed against the plate with a known force.

Since these tests are not capable of superseding the usual "practical" tests, the reader must be referred to the original papers.[4]

The practical examination of varnish for suitability and drying power is carried out in a similar fashion to that described above for boiled oils. The influence of the atmosphere (moisture, light, etc.) can only be observed by practically testing the varnishes as delivered to the trade, or after mixing them with pigments (see "Enamels").[5]

Enamels—Enamel Paints

French—*Peintures émail, laques à l'huile.* German—*Öllacke Emaillefarben.*

"Enamels" or enamel paints is a trade term given to mixtures of varnishes with pigments (such as zinc oxide, lead oxide, iron oxide, etc.). The name is due to the property of these preparations to dry with the production of a skin having an enamel-like gloss. The protection afforded by enamels is very much greater than that given by the corresponding paints containing no gum-resin.

The manufacturing process is similar to that for paints. The well-settled varnish oils are thoroughly ground up with finely levigated pigments until a homogeneous mass free from grit is obtained. Finally the mass is thinned with oil of turpentine. The finished product is carefully preserved from contact with air, so that no premature formation of a skin on the surface of the varnish may take place.

Black enamels of good quality are prepared with the aid of asphaltum without using a black pigment (charcoal), as the drying is greatly retarded by the presence of the latter.

For the chemical examination of enamel paints the methods described for the examination of paints and of varnishes must be combined.

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[1] Cp. Heupel, *Chem. Revue*, 1903, 125.
[2] *Journ. Royal Scottish Soc. of Arts*, 1906, xvii. 101.
[3] English patent 3486, 1906.
[4] Muckenfuss, *Journ. Ind. Eng. Chem.*, 1913, No. 7.
[5] Cp. also *Chem. Revue*, 1908, 119.

V.—OXIDISED OILS

French—*Huiles oxydées.* German—*Oxydierte Öle.*
Italian—*Olii ossidati.*

Under the term "oxidised oils" are comprised all those oils which have absorbed oxygen by exposure to the atmosphere, or have been oxidised artificially by heating ("blowing") in a current of air, oxygen gas, or ozone.

From the explanations given in Vol. I. Chap. VII., it will be gathered that only the semi-drying oils and drying oils lend themselves to the manufacture of oxidised oils, although all oils and fats, if blown with oxygen at an elevated temperature, become oxidised with formation of volatile acids and "oxidised" acids. This has been shown by the author to occur even in the case of "premier jus."[1] The behaviour[2] of blubber oils and liquid waxes is similar to that of the semi-drying oils. It is convenient to divide the oxidised oils into two classes, namely, those obtained from semi-drying vegetable oils, blubber oils, and liquid waxes, on the one hand, and those obtained from drying oils, on the other.

(1) OXIDISED OILS FROM SEMI-DRYING VEGETABLE OILS, BLUBBER OILS, AND LIQUID WAXES, BLOWN OILS

These oxidised oils (termed commercially "blown oils," "base oils," "thickened oils," "soluble castor oils," French—*huiles soufflées*, German—*geblasene Öle*) are prepared by heating vegetable semi-drying oils, blubber oils, or liquid waxes, in a current of air to a somewhat elevated temperature.[2] The vegetable oils, blubber oils, or liquid waxes are placed in a jacketed pan or cylindrical vessel, provided with a steam coil and stirring arrangement (somewhat similar to the apparatus shown in Fig. 8), so that the oil is agitated whilst the air is blown through it; the object of the agitation and spraying by the air current is to produce as complete a contact as is possible of the oil with air. Whilst air is blown through the oils, steam is sent through the coil so as to bring the temperature up to 70° C. or more, in some cases even to 110-115° C. The agitation and blowing is continued until the desired specific gravity is reached. During the blowing some volatile fatty acids escape, as also some insoluble acids, which are carried away mechanically by the current of air. In some cases the temperature rises beyond that of the steam used for heating, so that it is frequently required to cool the "blown" oil by passing cold water through the jacket of the pan or the coil of the vessel, as the case may be.

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[1] *Analyst*, 1899, 322. Cp. table 36 of *Laboratory Companion to Fats and Oils Industries.* Cp. also Blown Lard Oil, Vol. II. Chap. XIV. under "Lard Oil."

[2] H. A. Gardner, *Circ.* Nos. 68 and 74, Paint Manufacturers' Assoc., U.S.A., August and October 1919.

[3] English patent 13,519, 1911, Markel and Crosfield; cp. also de Hemptinne, German patent 236,294; Mitscherlich and Sprenger, German patent 263,656.

In consequence of this treatment the oils increase in density and in viscosity. They approach in these respects castor oil, but differ from it in that they are miscible with mineral oils in all proportions; hence the commercial term "soluble castor oil" has been given to them. They further differ from castor oil by their sparing solubility in alcohol.

The most prominent chemical change the oils undergo through "blowing" may be gathered from the following tables. Therein are collated a number of observations on oils which have been oxidised on a laboratory scale, together with the corresponding numbers of the original oils from which they have been prepared. (Cp. also the tables given in Vol. II. Chap. XIV. under the headings of the individual oils and liquid waxes.)

For oxidised oils prepared in the Laboratory, see tables, page 184.

Oxidised Cotton Seed Oil (Lewkowitsch)

	Original Oil.				Acetylated Oil.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
	Specific Gravity at 15·5° C.	Saponification Value.	Total Volatile Fatty Acids per Gram in terms of Milligrams, KOH.	Oxidised Acids. Per cent.	Saponification Value.	Insoluble Fatty Acids.	Apparent Acetyl Value.	True Acetyl Value.	Difference, V. – II.
Cotton seed oil . .	0·9250		0·1		200·2	95·7	7·7	7·6	
Cotton seed oil, blown 2 hours at 120° C. .	0·9262	194·3	2·88	0·51	203·9	94·8	14·2	11·32	9·6
Cotton seed oil, blown 4 hours at 120° C. .	0·9291	194·9	2·44	0·87	212·0	92·9	22·9	20·46	17·1
Cotton seed oil, blown 6 hours at 120° C. .	0·9350	196·1	4·60	0·94	215·2	91·9	30·0	25·4	19·1
Cotton seed oil, blown 10 hours at 120° C. .	0·9346	196·8	4·16	1·28	218·4	91·4	35·0	30·84	21·6

OXIDISED OILS PREPARED IN THE LABORATORY

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.			XIII.	XIV. = VIII. − (IV. + XIII.).			
Oil.	Specific Gravity at 15·5° C. (Water 15·5=1).	Free Acid calculated as Oleic.	Unsaponifiable Matter.	Saponification Value.	Iodine Value.	Specific Temperature Reaction.	Insoluble Acids.	Soluble Volatile Acids.	Soluble Non-Volatile Acids.	Iodine Value of Insoluble Acids.	Molecular Weight of			Oxidised Acids.	Non-Volatile Fatty Acids freed from Oxidised Acids and Unsaponifiable.			Observer.
											Insoluble Acids.	Soluble Non-Volatile Acids.	Soluble Volatile Acids.					
		Per cent.	Per cent.				Per cent.	Per cent.						Per cent.	Per cent.	Molecular Weight.	Melting Point °C.	
Rape	0·9141	5·10	0·65	173·9	100·5	135	94·76	0·52		...	...	...	...	...	...	...	...	Thomson and Ballantyne[1]
,, Blown 5 hours . .	0·9275	5·01	...	183·0	88·4	...	...	...	...	...	...	...	...	...	...	...	...	,,
,, Blown 20 hours . .	0·9615	7·09	0·76	194·9	63·2	...	85·94	9·20	0·82	66·5	327	241	72	...	...	...	...	,,
Sperm	0·8797	1·97	36·32	130·4	82·1	...	...	...	...	...	...	...	...	...	...	...	...	,,
,, Blown 25 hours . .	0·8989	3·27	34·65	142·3	67·1	...	...	...	...	...	...	...	...	...	...	...	...	,,
Cotton seed	...	1·1	1·05	190·4	108·8	...	94·22	...	...	...	...	...	...	0·27	92·9	278·1	35·36	Fahrion
Oxidised cotton seed obtained by exposure on chamois leather (Vol. I. Chap. VII.) and exhausting with petroleum ether—																		
After 8 days . . .	...	6·69	1·13	223·1	55·4	...	85·34	...	...	...	...	...	...	20·62	63·59	276·2	45·46	,,
After 12 days . .	...	6·94	1·33	227·5	46·3	...	83·62	...	...	...	...	...	...	19·13	63·16	273·2	46	,,
Oil obtained by subsequent exhaustion with ether of the leather extracted with petroleum ether	...	16·79	0·72	271·3	29·1	...	74·20	...	...	...	...	...	...	37·72	35·76	269·1	51	,,

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[1] *Journ. Soc. Chem. Ind.* 1892. 506.

SOME CHARACTERISTICS AND VARIABLES OF COMMERCIAL BLOWN OILS

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.		XV.	XVI.	XVII.	XVIII.
No.	Oil.	Specific Gravity at 15·5° C. (water 15·5=1).	Free Acid calculated as Oleic.	Unsaponifiable Matter.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Specific Temperature Reaction.[1]	Insoluble Acids.	Soluble Volatile Acids.	Soluble Non-Volatile Acids.	Iodine Value of Insoluble Acids.	Molecular Weight of		Oxidised Acids.	Apparent Acetyl Value.	True Acetyl Value.	Observer.
													Insoluble Acids.	Soluble Volatile Acids.				
			Per cent.	Per cent.					Per cent.	Per cent.	Per cent.				Per cent.			
1	Blown rape . . .	0·9672	4·93	2·80	197·7	...	63·6	253	84·97	1·90	1·94	62·7	296·0	104	...	...	...	Thomson and Ballantyne[2]
2	,, ,, . . .	0·9714	...	...	205·6	...	...	...	...	...	...	...	...	...	24·95	62·04	53·14	Lewkowitsch
3	,, ,, . . .	0·9772	8·5	...	163 (?)	...	47·2	...	...	...	...	...	...	...	...[3]	...	...	Lecocq and Dandervoort[4]
4	,, ,, . . .	0·9745	4·1	...	175·1	...	54·1	...	...	...	...	...	...	...	...[5]	...	...	
5	,, ,, . . .	0·9674	4·88	...	267·5	8·8	65·3	...	88·64	...	...	...	294·1	...	...	...	...	Gripper[6]
6	Blown Jamba . .	0·9169	...	0·65	174·9	...	99·5	...	95·90	...	...	...	311·0	...	0·53	...	...	Lewkowitsch
7	Blown cotton seed .	0·9740	3·38	1·00	213·2	...	56·4	227	...	...	...	...	...	...	...	...	...	Thomson and Ballantyne
8	,, ,, ,, .	At 20° C. (water 20°=1) 0·9722	...	...	213·7	...	...	...	...	...	...	...	...	...	26·45	65·6	48·54	Lewkowitsch
9	Blown seal . . .	0·9815	16·5	...	221·0	...	78·2	...	73·4	...	...	...	...	...	...	...	...	Chapman and Rolfe[7]

[1] Cp. Vol. I. Chap. VII.

[2] *Journ. Soc. Chem. Ind*, 1892, 506.

[3] Iodine value of the oxidised fatty acids, 36 ; neutralisation value, 191.

[4] *Bull. de l'Assoc. Belge de Chim*, 1901, 325.

[5] Iodine value of the oxidised fatty acids, 29·7 ; neutralisation value, 189.

[6] *Journ. Soc. Chem. Ind* 1899, 342.

[7] *Chem. News*, 1894 (70), 2.

A. *Characteristics of "Blown" Oils (Lewkowitsch)*

Blown Oil.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
	Acid Value.	Saponification Value.	II. – I.	Iodine Value.	Total Soluble Acids.	Specific Gravity.	Un-saponifiable.	Oxidised Acids.	Total Insoluble Acids.	Acetyl Value.		Saponification Value of the Acetylated Oil.	Insoluble Acids after Acetylation.	XII. – II.
										Apparent.	True.			
	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per cent.	Mgrms. KOH.		Per cent.	Per cent.		Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.		
Ravison rape	10·47	198·31	187·84	72·66	35·89	0·9685	1·23	21·22	83·52	88·37	52·93	243·2	...	44·9
East India rape	13·25	215·57	202·32	61·92	56·26	0·9623	0·93	20·74	82·18	102·87	46·61	253·33	...	37·76
Cotton seed	9·41	224·59	215·18	65·74	46·49	0·9785	1·37	29·39	82·59	110·73	64·29	273·30	83·85	48·71
Maize	7·33	208·63	201·30	90·7	49·13	0·9806	2·28	31·93	82·34	113·16	63·37	268·75	...	60·1

B. *Characteristics of the Mixed Fatty Acids (Lewkowitsch)*

Mixed Fatty Acids from	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
	Neutralisation Value.	Saponification Value.	II. – I.	Iodine Value.	Total Soluble Acids.	Total Insoluble Acids.	Acetyl Value.		Saponification Value of Acetylated Acids.	IX. – II.	Insoluble Acids after Acetylation.
							Apparent.	True.			
	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per cent.	Mgrms. KOH.		Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.		Per cent.
Blown ravison rape oil	175·14	191·7	16·56	73·31	7·26	...	50·0	42·75	227·4	35·7	...
Blown East India rape oil	171·93	190·0	18·07	60·80	10·71	...	66·2	55·5	237·8	47·8	...
Blown cotton seed oil	194·79	210·46	15·67	72·43	12·94	93·76	67·35	55·67	254·8	44·4	92·11
Blown maize oil	192·8	209·93	17·13	88·08	29·45	86·4	88·97	59·52	267·3	57·37	...

C. *Characteristics of Oxidised Acids (Lewkowitsch)*

Oxidised Acids from	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
	Neutralisation Value.	Saponification Value.	II. – I.	Iodine Value.	Total Soluble Acids.	Insoluble Acids.	Acetyl Value.		Saponification Value of Acetylated Acids.	IX. – II.	Insoluble Acids after Acetylation.
							Apparent.	True.			
	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per cent.	Mgrms. KOH.		Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.		
Blown ravison rape oil	171·5	208·0	36·5	49·14	22·56	...	102·5	80·0	307·5	99·5	...
Blown East India rape oil	173·3	211·3	38·0	39·79	22·35	...	128·0	105·65	315·9	104·6	...
Blown cotton seed oil	174·7	220·71	46·01	48·6	36·12	...	154·4	118·28	322·69	101·98	83·85
Blown maize oil	171·94	215·74	43·60	70·87	48·0	93·53	173·58	126·68	326·45	111·11	...

D. *Characteristics of Fatty Acids freed from Oxidised Acids (Lewkowitsch)*

Fatty Acids freed from Oxidised Acids from	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
	Neutralisation Value.	Saponification Value.	II. – I.	Iodine Value.	Total Soluble Acids, after Saponification.	Insoluble Acids.	Soluble Acids by Washing.	Acetyl Value.		Saponification Value of Acetylated Acids.	X. – II.	Insoluble Acids after Acetylation.
								Apparent.	True.			
	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per cent.	Mgrms. KOH.	Per cent.	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.		
Blown ravison rape oil	176·8	188·6	11·8	61·88	6·97	...	6·75	42·5	35·53	220·3	31·7	...
Blown East India rape oil	166·6	176·8	10·2	55·93	10·09	...	8·85	47·13	37·54	219·2	42·95	...
Blown cotton seed oil	188·0	196·15	8·15	56·02	11·0	...	7·27	33·69	22·69	232·0	33·6	96·17
Blown maize oil	172·37	177·68	5·31	85·52	6·14	85·54	7·54	43·8	36·7	228·76	50·52	...

The characteristics of the *blown oils* themselves are recorded in table A. On washing the acetylated oils with water, emulsions were formed, but the separation of the acetylated oil from the water caused no difficulty. The blown ravison oil gave the most persistent emulsion. The characteristics of the *mixed fatty acids* are given in table B. The *oxidised acids* (table C) were separated from the mixed fatty acids in the manner described in Vol. I. Chap. VIII. The saponification values of the oxidised acids are considerably higher than their neutralisation values; this proves that lactonic substances are present. On separating the lactones from the fatty acids in the manner described (Vol. I. Chap. VIII.), the supposed lactones were obtained as thick, viscous liquids, soluble in alcohol.[1] The fatty acids recovered from the soap solution were again found to contain notable quantities of lactones, apparently formed on liberating the acids from their soap solution. The lactones were again separated off in the same manner, and the soap solutions decomposed with mineral acid; the liberated fatty acids were again found to contain lactones. The comparatively high iodine values of the oxidised acids point to a considerable amount of unsaturated fatty acids. (Since the oxidised acids are practically insoluble in carbon tetrachloride, the determination of the iodine value was carried out in alcoholic solution. The error introduced thereby cannot have been a considerable one; for whilst the blank test with carbon tetrachloride required 50·6 c.c. of thio-sulphate, the alcoholic solution took 50·00 c.c.) Unlike the oxy-fatty acids of liver oils, those of cotton seed oil are completely soluble in ether. Contrary to expectation the oxidised acids contained also notable amounts of soluble fatty acids. The explanation which suggested itself, namely, that these soluble acids were formed by treatment of the oxidised acids with alcoholic potash, was not borne out by experiments, as the oxidised acids which had not been treated with alcoholic potash lost, on washing with water, considerable amounts of soluble fatty acids.

The characteristics of the *fatty acids freed from oxidised acids by* petroleum ether are detailed in table D. Their acetyl values are still considerable. It has not been ascertained yet whether this is due to the presence of hydroxylated acids soluble in petroleum ether. These acids also contain lactones (although their amount does not exceed 4 to 6 per cent), as well as small amounts of soluble acids.

These results show that the oxidised oils consist of a complicated mixture of acids. The nature of these acids is being investigated by the editor. Since the blown oils yield practically the full amount of glycerol, it would appear necessary to study in the first instance the influence of "blowing" on the individual unsaturated fatty acids—oleic, erucic, linolic. Hitherto oleic acid only has been examined, with the result tabulated (Vol. I. Chap. VIII.).

With the aid of the numbers given in the foregoing tables, taken in conjunction with such other characteristic tests as will readily suggest themselves to the analyst from the perusal of the sections "Cotton Seed Oil" and "Rape Oil" in Vol. II., the question can be easily solved, if required, as to whether a blown oil has been prepared from rape oil or cotton seed oil.

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[1] Cp. *Analyst*, 1902, 144.

In the examination of the oils it is advisable to determine the acetyl values of both the original oil and of its insoluble fatty acids.

The problem becomes more difficult if it be required to determine in a commercial lubricating oil the respective proportions of blown rape oil and blown cotton seed oil. A method based on the different amounts of ether-insoluble lead salts yielded by blown rape oil and blown cotton seed oil respectively (Vol. II. Chap. XIV.) is not likely to lead to satisfactory results, although a high iodine value of the fatty acids derived from the ether-insoluble lead salts would point to the presence of erucic acid and inferentially of rape oil. More information would be derived by ascertaining the melting points of the fatty acids, such as are described in table D of page 187, and perhaps by passing these acids through the lead-salt-ether method. *Marcusson*[1] is of the opinion that the different behaviour to petroleum ether of the fatty acids recovered from the ether-insoluble lead salts of the blown oils may furnish some clue. His numbers are set out in the following table :—

Kind of Oil.	Fatty Acids obtained from Lead Salts, insoluble in Ether.		
	Total Amount.	Acids soluble in Petroleum Ether.	Acids insoluble in Petroleum Ether.
	Per cent.[2]	Per cent.[2]	Per cent.[2]
Commercial blown rape oil .	1·2	1·2	0·0
,, ,, ,, .	14·5	5·7	8·8
Blown rape oil prepared in the laboratory	20·6	8·7	11·9
Commercial blown cotton seed oil	32·9	23·3	9·6
Blown cotton seed oil prepared in the laboratory . . .	45·8	32·5	13·3

The blown oils prepared from maize, cotton seed, rape, jamba, ravison oils, and to some extent also these obtained from seal and sperm oils, find technical application as lubricating oils in admixture with other oils. They are said to be useful for lubricating purposes on account of their high specific gravities and viscosities. Opinions differ, however, as to their suitability, objection being taken to them on account of their liability to "gum" and their low flash points. Nevertheless, the blown oils are extensively used in admixture with mineral oils and even with rosin oils.[3] The so-called "marine oils" used to contain considerable proportions of blown oils.

The longer fatty oils are "blown," the less becomes their miscibility with petroleum hydrocarbons. *Jenkins*[1] pointed out that the blown oils are least soluble in American petroleum hydrocarbons, more soluble in shale hydrocarbons, and comparatively easily soluble in the hydrocarbons from Russian petroleum. Greater still is their solubility in Borneo oils.

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[1] *Mitt. K. Mater.-Prüfungsamt*, 1905 (23), 47 ; *ibid.*, 1911 (29), 50.

[2] The percentages refer to the weight of oil used for the preparation of the lead salts.

[3] The employment of blown oils for the manufacture of putty is claimed by Horn (German patent 154,220). The application of oxidised oils in the production of solid fuel (for binding coal dust) is claimed by R. Middleton (English patent 347, 1905).

It may perhaps be possible to base a method of differentiating the various hydrocarbons on their different behaviour with oxidised oils.

The blown oils obtained from fish, liver, and blubber oils were hitherto almost exclusively prepared for, and used in, the leather industries. These oils will, therefore, more suitably be described under the heading of " Sod Oil " and " Dégras " (Chap. XVI.). At present, however, blown fish and blubber oils are admixed to mineral oils. The admixture of lubricating oils is practised to a notable extent.

(2) Oxidised Oils from Vegetable Drying Oils

If vegetable drying oils are exposed to the atmosphere, or to a current of air, at a somewhat elevated temperature, the formation of oxidised acids proceeds much more rapidly than in the case of semi-drying oils.

Extensive use is made of this property in the application of paints and varnishes. The vegetable oil—chiefly linseed oil[2]—finally dries to a solid mass, which forms a coherent coat on the surface of the object to which a paint or varnish has been applied.

The drying oils absorbs also ozone[3] readily with the formation of " ozonides." It is doubtful whether the " ozonides " are stable at the temperatures at which ozonised oils are prepared. At any rate, the " ozonised oils " (see p. 152) prepared by blowing at an elevated temperature with ozonised air seem to differ from " oxidised " oils.

The theories which have been propounded hitherto to explain the " drying " can only be referred to here briefly, inasmuch as they do not yet furnish a completely satisfactory explanation.

The chemical change which takes place when a vegetable oil " dries " to a solid elastic skin, is but very imperfectly understood. The final product appears, however, to be the same, whether raw linseed oil be allowed to absorb oxygen from the atmosphere slowly, whether the " drying " be accelerated by previously converting the oil into " boiled " oil, or if the raw linseed oil be treated in a current of oxygen or ozone at a somewhat elevated temperature, after having been intermixed with driers. *Mulder's* opinion that in the first stage the glyceridic constituent of the oil is oxidised and that the liberated fatty acids take up oxygen and are converted into the anhydride of " hydroxylinoleic " acid (*i.e.* the anhydride of hydroxylated linseed oil fatty acids), a neutral substance, insoluble in ether, termed by him " linoxyn," must be rejected as erroneous, for this view postulates that hydrolysis of the glycerides precedes oxidation. It has been pointed out already that the solid skin is not formed when the mixed fatty acids are exposed to the atmosphere. Moreover, *Bauer and Hazura*[1] have shown that at any rate in the first stage of oxidation the glyceridic constituent of the linseed oil remains intact, and that the oil is converted by exposure in thin layers into a substance simulating in its properties *Mulder's* "linoxyn," but still representing a glyceride. This substance was assumed by *Bauer and Hazura* to be hydroxylinolein (*i.e.* a mixture of hydroxylinolin and hydroxylinolenin). α-linolenic acid on oxidation absorbs 51·4 per cent of oxygen. Since this corresponds to nine atoms of oxygen per molecule, it is evident that *S. Coffey*[2] had obtained a product analogous to "superoxidised" oil. This is more clearly shown by the fact that carbon dioxide and acetic acid were observed among the volatile products of degradation. Linolic acid, on the contrary, when oxidised yielded no volatile matter.

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[1] Cp. *Analyst*, 1902, 145.

[2] With regard to tung oil, cp. Kronstein, English patent 1386, 1901.

[3] Cp. *Chem. Zeit.*, 1891, 672.

Fahrion[3] applied *Engler and Weissberg's*[4] autoxidation theory to this problem, and in the light of this theory he regards the linseed oil as an "acceptor," and the driers, especially lead and manganese, which are readily converted into peroxides, as autoxidisers or catalysers. He further argues that some facts seem to show that the drying process may also be considered as a molecular autoxycatalysis, and driers can then only be looked upon as pseudo-catalysers (pseudo-autoxidisers), they causing the addition of hydroxyl groups, and leading to the formation of a secondary autoxidiser. The latter in its turn would take up oxygen in its molecular form, and become converted into a hydroperoxide, which finally is decomposed by water into the hydroxide of a metal and hydrogen peroxide.

The phenomena occurring whilst a paint which has been thinned with turpentine or an ordinary varnish dries can be easily summarised under this theory. Oil of turpentine absorbs oxygen from the air (this phenomenon is termed "autoxidation"), and, judging from the iodine value, oil of turpentine should be able to absorb two molecules of oxygen. Whether these are present in the form of oxygen or of ozone, or partly as oxygen and ozone, does not appear settled yet. The oxygen "activated" by the oil of turpentine (and contained in old oil of turpentine to a considerable extent) is, according to *Engler and Weissberg*,[4] neither ozone nor atomistic oxygen, nor (as stated by *Kingzett*[5]) hydrogen peroxide. The oxygen is said to have been taken up in molecular form, with the formation of a peroxide, which, by intramolecular rearrangement, is either changed to an ordinary oxide or disappears owing to its having oxidised some of the as yet unchanged molecules of the oil.

If the views of *Engler and Weissberg* are accepted, then the well-known fact that turpentine absorbs ozone rapidly would have to be looked upon as an entirely different reaction, and the question whether oil of turpentine absorbs oxygen from the air, or is able to " activate " it into ozone, would, in the author's opinion, have to be decided ultimately by isolating the oxidation products obtained in either case. An important step in this direction has been made by *Harries and Neresheimer*,[1] who have shown that on passing ozonised air through oil of turpentine 10-20 per cent of a solid pinene ozonide (" pinene perozonide ") and 90-80 per cent of a liquid pinene-ozonide are obtained. The solid pinene ozonide does not appear to have a constant composition, but to correspond to a mixture of $C_{10}H_{16}O_4$ and of $C_{10}H_{16}O_3$.

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[1] *Monatsh. f. Chem.*, 1888 (9), 459; *Zeits. f. angew. Chem.*, 1888, 455.

[2] *Chem. Soc. Trans.*, 1921, 119, 1408.

[3] *Chem. Zeit.*, 1904, 1196.

[4] *Kritische Studien über die Vorgänge der Autoxydation*, Braunschweig, 1904. Cp. also Fokin, *Journ. Russ. Phys. Chem. Soc.*, 1907, 609; 1908, 276; *Zeits. f. angew. Chem.*, 1909, 1451; 1492.

[5] *Journ. Chem. Soc.*, 1874, 511; 1875, 210; cp. also Kingzett and Woodcock, *Journ. Soc. Chem. Ind.*, 1912, 265.

The main product of the reaction is optically active, and has the formula $C_{10}H_{16}O_3$. (Perhaps further investigations may enable us to isolate also the " peroxides " of oil of turpentine.)

In the light of *Engler and Weissberg's* theory, oil of turpentine, when absorbing oxygen from the air (" autoxidation ") would act as an " acceptor." Oil of turpentine is capable of absorbing dry oxygen; hence the process can take place in the absence of moisture. If the autoxidation of the oil of turpentine occurs in the presence of water, the latter reacts subsequently on the peroxide (which is assumed to have been formed) with the formation of an oxidation product and of *hydrogen peroxide*. As may be expected, paints thinned with petroleum hydrocarbons exhibit inferior drying properties.[2]

In the presence of oxidisable substances, such as linseed oil in paints, or linseed oil and gum-resins in varnishes, oil of turpentine would appear to act as a pseudo-autoxidiser (pseudo-catalyser), it being taken as granted that linseed oil itself does not appear to behave as an auto-acceptor, since raw linseed oil does not contain peroxides.

Experimental data favouring *Engler and Weissberg's* view have been furnished by *Genthe*.[3] In an elaborate physico-chemical study of the drying of linseed oil he has shown by a series of experiments that the drying process would appear to represent a special case of auto-catalysis, inasmuch as his results correspond, approximately, to numbers obtained by means of the equation $dx\ dt=k(m-x)\ (a-x)$ (the equation propounded by *Ostwald*) for auto-catalytic reactions). The substance which acts as the auto-catalyst could, however, not be isolated, and the assumption is made that it has the character of a peroxide. The so-called " blown boiled oils " would therefore be linseed oils, in which peroxides are pre-formed, and the accelerating action which old oil of turpentine possesses would be due to the high percentage of peroxide. (It must, however, not be overlooked that the peroxide has not yet been isolated, and that hydrogen peroxide does not accelerate catalytically the process of drying, as *Genthe* himself has shown.[4]) The " driers " would thus have to be considered as pseudo-catalysts, their function being to accelerate the drying process by assisting in the formation of the auto-catalysers (" peroxides "). *Orloff*[1] gives experimental data agreeing in the main with *Genthe's* theory.

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[1] *Berichte*, 1908, 38.

[2] Power, *Analyst*, 1910, 192.

[3] *Zeits. f. angew. Chem.*, 1906, 2087.

[4] With regard to benzoylperoxide, cp. Prileschajew, *Berichte*, 1909, 4811.

In this connection it may be pointed out that *Genthe* patented[2] a process which purports to pre-form " peroxides " in linseed oil by exposing it to ultra-violet light (" Uviol light "), or by oxidising linseed oil electrolytically with the aid of lead electrodes.[3]

Ostwald and Ostwald[4] claim to be able to regulate the process of autoxidation of linoleum, rubber, etc., in such a manner as to prevent the degradation of the finished article, by the addition of a neutral or basic aromatic compound containing nitrogen.

Genthe states that at the same time as oxidation takes place polymerisation occurs, as is ascertained by the determination of molecular weights.[5] It would appear, however, to the author[6] that this must not be accepted as proven, since at the temperature to which the oil was heated, viz. 135° C., polymerisation of linseed oil does take place, independently of oxidation ; and it must further be pointed out that *Genthe* has not shown experimentally that polymerisation occurs at the ordinary temperature, at which, as is well known, oxidation proceeds at a very distinct although slow rate.[7]

Fahrion has shown that when boiled oils dry, part of the fatty acids is converted into a class of acids for which the author suggested the name " oxidised " acids. The oxidised acids are formed to a moderate extent only during the process of " boiling " linseed oil (cp. p. 205). On spreading three boiled oils (of the iodine values 101·3, 77·3, 33·7, and containing 0·5, 4·1, 7·6 per cent of oxidised acids respectively) in a thin film on a glass plate, and exposing the oils to the air for ten days at a somewhat higher temperature than the ordinary, *Fahrion* found that the proportions of oxidised acids had increased to 30·6, 20·8, and 16·4 per cent respectively.[8]

It appears likely that in the first instance the linolenic acids are attacked, and that the linolic acid only plays a subordinate part ; otherwise maize and cotton seed oils would exhibit better drying powers than they actually possess.

With a view to investigating the changes which take place when linseed oil dries, the author treated linseed oil at 120° C. with air for a varying number of hours, or, in other words, prepared " blown " linseed oils. The results obtained on examining the products are set out in the following table :—

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[1] *Journ. Russ. Phys. Chem. Soc.*, 1911, 1509. Cp. also H. Ingle, *Journ. Soc. Chem. Ind.*, 1917, 319.

[2] German patent 195,663. Cp. also above, p. 145.

[3] The formation of ozone by ultra-violet light has been proved by Lenard, *Ann. d. Physik*, 1900 (I) 486 ; cp. F. Fischer, *Berichte*, 1909, 2228 ; E. v. Aubel, *Compt. rend.*, 1909 (149), 983.

[4] English patent 10,361, 1910.

[5] Cp. G. Borries, *Beiträge zur Kenntniss des Trocknens von Ölen*, Inaug. Dissert., Zwickau, 1902.

[6] *Jahrbuch d. Chem.*, 1906, xvi. 407.

[7] For some objections raised by Fokin against Genthe's views see *Zeits. f. angew. Chem.*, 1909, 1453.

[8] Cp. also W. Fahrion, *Chem. Umschau*, 1921 (28), 5, 20.

Characteristics of Oxidised (“ Blown ”) Linseed Oil (Lewkowitsch)

	Oxidised Oil.				Acetylated Oil.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
	Specific Gravity at 15·5° C.	Saponification Value.	Total Volatile Fatty Acids in terms of Milligrams, KOH.	Oxidised Acids. Per cent.	Saponification Value.	Insoluble Acids.	Apparent Acetyl Value.	True Acetyl Value.	Difference, V. – II.
Linseed oil	...	...	0·8	...	205·6	96·2	12·5	11·7	...
Linseed oil, blown 2 hours at 120° C.	0·9334	189·8	1·68	1·2	200·9	94·4	18·9	17·22	11·1
Linseed oil, blown 4 hours at 120° C.	0·9403	191·3	3·0	1·7	203·9	94·6	22·5	19·5	12·6
Linseed oil, blown 6 hours at 120° C.	0·9446	192·4	8·3	5·03	208·2	93·2	25·5	17·2	15·8
Linseed oil, blown 10 hours at 120° C.	0·9460	192·7	0·9	7·1	211·8	92·1	32·6	31·7	19·1

If the oxidation of linseed oil is carried further, until the oil has taken up the maximum amount of oxygen, a flexible solid mass is obtained, termed " solidified (linseed) oil," " solid linseed oil," " oxidised linseed oil " (" linoxyn ").

By heating " linoxyn " with methyl- and ethylalcohol dark-coloured solutions are obtained, owing to decomposition of the " linoxyn." Amylalcohol and amylacetate dissolve " linoxyn " at the ordinary temperature after standing for some prolonged time. The mass swells up at first with complete absorption of the solvent; in course of time the mass liquefies, and after about a year a clear transparent solution is obtained. From this solution the original " linoxyn " can be recovered by spontaneous evaporation of the solvent. *Berlaimont*[1] claims to prepare varnishes by dissolving " linoxyn " and oleo-resins (without previous " running ") in amyl alcohol and amyl acetate.

Leeds examined two oxidised oils which were obtained by treating linseed oil with oxygen in a jacketed pan. They are contrasted in the following table with a sample of completely dried oil obtained from a raw linseed oil exposed in a flat dish to a moderate current of air at 45° C. for about five weeks, the skin formed being daily broken up and intermixed with the bulk. This dried linseed oil had a jelly-like consistence, lumps of comparatively hard material and skin alternating with a small quantity of oil, of the consistence of " middle " varnish :—

Oxidised Linseed Oil prepared by Treatment with Oxygen

Oils.	Specific Gravity at 15° C.	Free Acid calculated as Oleic Acid.	Saponification Value. Mgrms. KOH.	Unsaponifiable Matter.	Oxidised Acids.	Iodine Value.
		Per cent.		Per cent.	Per cent.	
Oxidised oil, weak	1·03	18 - 28·4[2]	221	0·89	42·82	58·8
„ „ strong	1·05	18·49-28·9[2]	223·5	0·97	44·19	53·5
Dried linseed oil .	...	12·67	171·6	0·81	31·58	93·9

Mixed Fatty Acids.	Melting Point.	Solidifying Point.	Mean Combining Weight.	Saponification Value.	Iodine Value.
	°C.	°C.			
Oxidised oil, weak .	28	26	241·4	232·4	63·2
„ „ strong .	27	25	242·5	231·3	60·6
Dried linseed oil .	26	22	268·8	208·7	100·3

The fact that oxidised linseed oil absorbs considerable amounts of oxygen during " blowing " is brought out by the following elementary analyses due to *Williams*[3] :—

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[1] German patent 233,335.

[2] The first of these figures was found when the pink colour of the phenolphthalein remained after a vigorous shaking; but it disappeared after a short time, and more alkali was run in until the pink colour remained constant for two or three minutes; thus the second figure was obtained (cp., however, *Journ. Soc. Chem. Ind.*, 1890, 849).

[3] *Analyst*, 1898, 253.

	Carbon.	Hydrogen.	Oxygen.
	Per cent.	Per cent.	Per cent.
Solid oil I.	74·32	10·04	15·64
,, II.	69·74	9·57	20·69
,, III.	69·52	9·49	20·99
,, IV.	64·74	9·01	26·25
,, V.	65·40	9·00	25·60
,, VI.	68·64	9·24	22·12
,, VII.	64·38	9·01	26·61
Raw oil	75·03	10·78	14·19
,,	75·40	10·64	13·96

The solid oil is notable for its high amount of oxidised acids.[1] A few characteristics of the oxidised acids prepared from solidified linseed oil have been given above (Vol. I. Chap. VIII.). In the following table are collated the results obtained in the examination of a solidified oil.[2]

Characteristics of Solid Linseed Oil (*Linoleum Mass*) *and its Acids* (*Lewkowitsch*)

		Solid Oil.	Total Fatty Acids.	Oxidised Acids.	Fatty Acids freed from Oxidised Acids.
I.	Neutralisation value	...	209·63	...	179·97
II.	Saponification value	287·47	248·74	...	187·58
III.	II. – I.	...	39·11	...	7·61
IV.	Iodine value	52·2[3]	60·27	46·49	61·31[4]
V.	Total soluble acids, per grm. of substance, mgms. KOH	136·9	59·57	59·68	18·89
VI.	Unsaponifiable, per cent	1·33	...	...	...
VII.	Oxidised acids, per cent	53·01	...	...	...
VIII.	Insoluble acids + unsaponifiable, per cent.	53·92	81·32	...	...
IX.	Apparent acetyl value	...	115·01	164·67	50·25
X.	True acetyl value	...	55·04	104·99	31·36
XI.	Saponification value of the acetylated product.	367·75	304·24	341·43	246·11
XII.	Insoluble acids after acetylation, per cent.	...	84·4	76·38	96·05
XIII.	XI. – II.	...	55·5	86·29	58·53

Further investigation is required to elucidate the changes which linseed oil undergoes whilst being converted into solid oil.

The following figures are given by *Fritz and Zymandl*[5] :—

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[1] Fahrion, *Zeits. f. angew. Chem.*, 1910, 1107.

[2] Lewkowitsch, *Analyst*, 1902, 140.

[3] This was determined in glacial acetic acid, for although a highly oxidised linseed oil is not completely soluble in this solvent, it disintegrates, and this solvent is to be preferred to chloroform or carbon tetrachloride. Cp. also Meister, *Chem. Revue*, 1910, 260.

[4] These acids were soluble in petrol ether and their lead salts were soluble in ether. The acids could be resolved by means of the lead-salt-ether method into solid acids—iodine value 6·8; liquid acids—iodine value, 105·3. These liquid acids contained, according to Fahrion, only traces of linolenic acid and would, according to a calculation from the iodine value, consist of about 20 per cent linolic and 80 per cent oleic acid.

[5] *Chem. Revue*, 1914, 21.

	Consistence.	Specific Gravity compared with Water at 4° C.	Iodine Value (Wijs).	Ash.	Unoxidised Fatty Acids.	Oxidised Fatty Acids.	Water soluble Fatty Acids.
				Per cent.	Per cent.	Per cent.	Per cent.
Oil prepared by the Walton process (4 samples)	Hard	1·0862 at 15° C. to 1·0734 at 21° C.	61·8-65·5	1·16-1·41	26·2-31·2	46·4-56·4	5·5-8·6
Rapidly oxidised oil (2 samples)	Very soft	...	96·2 (1)	0·15 (1)	43·5-49·4	42·1-42·5	2·7-5·7

Solidified oil is heavier than water; it is practically insoluble in ether, chloroform, and carbon bisulphide. On a large scale this substance is prepared by three methods. The first consists in allowing linseed oil (previously "boiled" with a drier in order to accelerate the oxygen absorption) to run over "scrim," a light cotton fabric hanging down from the ceiling of a high building, the temperature of which is kept at about 100° F. A portion of oil solidifies on the fabric; the oil which drains off is again pumped up and allowed to run down until the layers of the semi-solid mass have reached (after several weeks) the thickness of about half an inch. This process is termed the "scrim process"; the solidified oil obtained by this method is termed "scrim oil."[1] This scrim oil represents a colloidal solution.

The second method consists in passing a current of oxygen gas through linseed oil intermixed with a drier and heated by steam in jacketed pans.[2] When the maximum amount of oxygen has been absorbed, the mass forms a thick viscous fluid, which will still flow whilst hot, but on cooling solidifies to a substance similar to the "scrim oil." During the "blowing" partial hydrolysis and oxidation of the glycerol formed takes place, as notable quantities of acrolein vapours escape. The semi-solid oil so obtained has not the same elastic properties which the "scrim oil" possesses. This is no doubt due to the fact that in the scrim oil the destruction of glycerol is much smaller, and the oxidation does not proceed so far as to form "super-oxidised oil" (see below). Whether these two kinds of solid oil are identical in their composition, and furthermore, whether they are identical with the elastic skin obtained when "boiled oil" dries, has not yet been ascertained.

Both processes were invented by *F. Walton* (in 1860 and 1863).

In another process, known as the *Taylor-Parnacott* method, the linseed oil is thickened at a high temperature in a current of air. This process requires only a few hours, and would seem to be in the main a polymerisation process. The oil is converted into an elastic, dark, rubber-like mass, and is used (like the two kinds of oxidised oils obtained by *Walton's* processes) for the manufacture of "corticine." The *Taylor-Parnacott* process, invented in 1871, proved for some time a competitor to the *Walton* processes. Solidified oil obtained by this process is lacking in tenacity and is also deficient in covering power, for, whereas solidified oil prepared by the two preceding methods need only form 30 per cent of the linoleum, cement prepared by the *Taylor-Parnacott* process will take up very little more than its own weight of filling materials. It is, however, suitable for the manufacture of "cork carpets," which consist of the cement mixed with coarse cork and very little pigment. Owing to its freedom from rosins it is possible to sand-paper (buff) the surface of the cork carpet (*de Waele*).[3]

According to *A. Genthe*[4] a solidified oil, for which a superiority is claimed over "scrim oil," is obtained by preparing a colloidal solution of a rapidly oxidised oil in raw linseed oil.

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[1] A laboratory apparatus for the practical demonstration of the manufacture of "scrim oil" has been described by Limmer, *Zeit. f. Chem.*, Apparat, 1907, 399.

[2] Bedford, German patent 83,584. Cp. Brin, English patents 10,968, 12,652, 1886.

[3] Private communication.

[4] German patent 229,424; English patent 1990, 1909; French patent 398,804.

A. Kronstein claims to obtain an alkali-resisting linoleum by using polymerised tung oil [1] or linseed oil previously freed from solid glycerides. *Friedemann* [2] patents the preparations of a soluble body from linoxyn by treating the linoxyn with boiling acetic acid and evaporating off the acid. Latterly attempts have been made to use the acids of linseed oil in place of the glycerides.[3]

Linoleum

The solid linseed oil is used on an extensive scale in the manufacture of **linoleum.**[4] For this purpose the solidified oil is ground to a coarse powder and placed in a steam-jacketed pan, fitted with a stirring gear, together with rosin, or, in the case of the most expensive linoleum, kauri gum.[5] The contents of the pan are gradually raised to 150° C., whereby the mixture is "run down" first to a liquid, which after a time becomes stiff. The mass is then run off into thin layers termed *linoleum cement.* It is rolled on to a jute canvas-backing, and is finally stoved—"seasoned"—at a temperature of 75° F. (120°-140° F.) [6] before being placed on the market in its well-known form.[7] The "linoleum corticine" produced by the *Taylor-Parnacott* process requires a second "seasoning." The addition to a linoleum of sodium bicarbonate is claimed to render it fire-proof.

Besides plain and printed linoleums, there are also manufactured at present "inlaid linoleum" and "cork carpet." [8] Detailed indications as to their manufacture fall outside the scope of this work. A comprehensive account of the history and manufacture of linoleum is given by *M. W. Jones.*[9]

The valuation of linoleum is almost exclusively based on "practical" tests. The methods employed for testing linoleum at the Kön gliche Technische Versuchs-Anstalten [10] embrace determinations of specific gravity, weight per square centimetre, thickness, resistance to wear, bending tests over mandrils of 10 to 45 mm. diameter, tensile strength, extensibility, permeability to water and the action of weak acids, alkalis, and petroleum.

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[1] Cp. German patents 180,621, 204,398; Nördlinger, *Chem. Fabrik Flörsheim,* German patent 251,371.

[2] German patent 258,853.

[3] Patent application 2057, 1918 (Barry and Barry, Ostlere and Shepherd). English patent 123,791, 1918 (A. B. Craven and The Yorkshire Dyeware and Chemical Co., Ltd., Leeds).

[4] Cp. W. F. Reid, *Journ. Soc. Chem. Ind.,* 1896, 75.

[5] Polymerised wood oil, "rubber rosin," and spirit soluble gums have been suggested as substitutes for the more expensive kauri gum, but they yield cements lacking in elasticity and durability. (A. de Waele.)

[6] De Waele. Cp. also de Waele, *Journ. Ind. Eng. Chem.,* 1917, 9, 6.

[7] In order to render linoleum non-combustible, the Società del Linoleum, Italy, claims (French patent 382,279) a mixture of 23 parts of linoleum cement, 20 parts of cork meal or wood meal, 6 parts of precipitated silica, 8·4 parts of sodium bicarbonate, 42 parts of natural magnesite, 6 parts of ochre (or another mineral pigment). The jute backing on to which this mixture is rolled is steeped in a solution of ammonium chloride, boric acid, and borax.

[8] Ingle, *Journ. Soc. Chem. Ind.,* 1904, 1201.

[9] *Journ. Soc. Chem. Ind.,* 1919, 26 T.

[10] Burchartz, *Mitth. Königl. Tech. Vers.-Anst.,* 1899, 285.

Ingle has criticised these methods and shown that the mechanical (practical) methods of examination must be adapted in each special case to the use to which the linoleum is to be put. Thus the testing of tensile strength would appear absolutely useless, as linoleum is not subjected to any stretching strains.

The following chemical tests may prove useful (*Ingle*) :—

(1) *Determination of Ash.*—Inlaid linoleum gives the highest percentage of ash. A linoleum containing above 20 per cent of ash is apt to be brittle. The ash includes, of course, the amounts of pigment used in the manufacture of the linoleum, as also the metals contained in the drier.

(2) *Extraction with Ether.*—The extraction with ether and the determination of the ether-soluble proportion does not afford satisfactory guidance. For not only would the non-oxidised or non-oxidisable portion of the linseed oil pass into the ether extract, but so also would the gum-resins and any rosin used in the manufacture of the cement. In addition to this, the ether-soluble constituent of the cork (which may reach 4·5 per cent) would pass into the ether extract together with the gum-resins (and rosin). If linoleum is made solely from polymerised linseed oil (*Taylor-Parnacott* process), then only the non-oxidised portions of the linseed oil and the cork extract will be found in the residue left after evaporating off the ether. *Ingle* thus obtained from a *Taylor-Parnacott* cement made from polymerised oil and cork only 8 to 10 per cent of extract. But if the cement be afterwards mixed with rosin, then the ether-extract may amount to almost 18 per cent. Linoleum made by *Walton's* processes gives a larger amount of ether-extract—from 16 to 23 per cent of ether-soluble extract—than that made by *Taylor-Parnacott's* process. It is evident that two linoleums made from different kinds of cements must not be compared on the basis of the ether-extract.

(3) *Determination of Moisture.*—Moisture is determined by drying for one hour in the water oven. This test is considered of importance by *Ingle* as " it reveals the amount of surface presented by a given weight of linoleum, and hence is more or less proportional to its porosity."

(4) *Water Absorption Test.*—In order to carry out this test, the canvas back must be removed and the linoleum back thus laid bare, rasped smooth with a file. A piece of linoleum of about 50 square cm. surface is dried in the water oven and weighed. The drying opens up the pores for the freer action of the water. The dried linoleum is placed in water for a definite period, taken out, dried between filter paper, and weighed. The increase in the weight (amount of water absorbed) affords a clue in the valuation of linoleum. This test would be best carried out side by side with a number of linoleums of known quality. A large amount of water absorbed means high porosity, and this would seem to indicate that the granules of the linoleums are not adhering sufficiently, and can therefore be more easily removed by wear. For more detailed information the reader must be referred to the original paper and to the following table :—

Examination of Linoleums (Ingle)

No.	Kind of Linoleum and Cement used.	Weight per Square Inch in grms.		Total Thickness in mm.	Linoleum Thickness in mm.	Moisture present.	Ash Content.	Ether Extract.	Water Absorption in			
		Total.	Linoleum only.						24 Hours.	48 Hours.	15 Days.	7 Weeks.
	Plains—					Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Oxidised oil	2·29	2·03	3·6	3·10	1·3	13·6	19·5	2·2	2·9	7·4	12·6
2	” ”	2·47	2·07	3·3	2·70	1·46	24·2	16·9	2·5	3·5	10·4	18·0
3	” ”	2·60	2·21	3·7	3·15	1·60	17·65	18·2	2·2	2·9	7·4	12·6
4	Polymerised oil[1]	2·42	2·01	3·6	3·1	1·58	14·9	17·8	2·7	3·7	10·2	17·2
5	Oxidised oil	3·30	2·87	4·8	4·4	1·30	15·1	...	2·5	3·3	8·5	14·5
6	” ”	1·50	1·27	2·2	1·75	1·5	18·1	17·7	3·7	4·9	12·0	18·5
7	” ”	1·52	1·15	2·2	1·80	2·5	10·5	23·3	7·3	9·5	20·0	30·5
8	Polymerised oil[1]	1·52	1·08	2·2	1·75	2·5	?	...	5·5	7·1	15·8	20·3
	Cork Carpets—											
9	Polymerised oil[1]	2·65	2·35	7·4	7·1	1·78	7·6	...	7·8	10·8	29·0	43·5
10	Oxidised oil	3·52	3·24	7·05	6·65	1·26	14·9	...	3·75	4·6	16·2	24·5
11	” ”	2·70	2·34	5·35	4·8	2·2	13·3	22·3	8·0	10·5	27·5	46·2
	Printed Linoleum—											
12	Oxidised oil	2·53	1·90	3·7	2·9	1·6	...	...	3·45	4·75	11·0	...
	Inlaids—											
13	Oxidised oil cement	2·56	1·7	3·15	2·2	1·7	15·8-34 per cent.	17-19·5 per cent.	4·8	6·3	16·0	21·5
14	” ”	2·48	1·54	3·10	2·1	1·85			...	8·5	18·0	...
15	” ”	2·28	1·65	3·0	2·3	1·5			3·0	5·5	11·9	...
16	” ”	1·98	1·25	2·45	1·7	1·4			5·4	7·1	17·7	24·2
17	” ”	1·64	0·93	2·1	1·2	1·6			7·3	9·8	21·3	26·5
18	” ”	2·35	1·88	2·9	2·45	1·46	16·18-29 per cent.	19-22 per cent.	...	8·3	18·0	...
19	” ”	1·53	1·03	2·15	1·45	2·6			...	16·0	28·5	...
20	” ”	2·25	1·70	3·0	2·5	2·25			...	16·0	23·6	...
21	” ”	2·91	2·10	3·6	2·7	1·96			...	12·9	23·5	...
22	” ”	2·10	1·41	2·8	2·15	4·1			...	23·4	32·3	...
23	” ”	1·98	1·51	2·7	2·15	2·6			...	18·0	26·5	...
24	” ”	2·68	1·54	3·55	2·40	4·3			...	26·4	37·0	...

[1] *Taylor-Parnacott* process.

Reid[1] showed that the "solid oil" is liable to still further oxidation, for he obtained from it a viscous liquid, heavier than water, and soluble in it to a considerable extent. This liquid is termed by *Reid* "super-oxidised" linseed oil. The decay which paints and varnishes exposed to the atmosphere undergo in course of time may be explained by the formation of this super-oxidised oil, which is washed away by rain water. Linoleum would appear to undergo the same change at a much slower rate. The investigation of the "super-oxidised oil" is desirable.

With regard to linoleums made from polymerised tung oil, cp. p. 137. *Reif*[2] prepares linoleum substitutes from vulcanised oils.

VI.—VULCANISED OILS, RUBBER SUBSTITUTES

French—*Caoutchoucs factices.* German—*Kautschuksurrogate, Faktis.* Italian—*Olii vulcanizzati.*

The action of sulphur chloride on oils and fats has been discussed in Vol. I. Chap. VII.; it has also been pointed out that a considerable amount of heat is evolved when sulphur chloride interacts with oils and fats.

The action of sulphur on oils and fats is much slower. At the ordinary temperature no chemical change takes place; at elevated temperatures, however, sulphur does react with the oils and fats in a manner that may be likened to the absorption of oxygen at the ordinary temperature. The products obtained by the reactions are solid bodies which possess some degree of elasticity, and are therefore used as rubber substitutes.

The manufacture of these substitutes is carried out in a manner simulating the vulcanising of india-rubber, namely, either by treating oils with sulphur at a somewhat elevated temperature (comparable to the "hot cure" of vulcanising india-rubber), or by treatment with sulphur chloride in the cold (corresponding to the "cold cure" in the vulcanising of india-rubber). Hence the term "vulcanised oils" is appropriately applied to these products.

According to the process used, the vulcanised oils are differentiated in the trade as "brown" (black) and "white substitutes" respectively. The "white substitutes" contain, therefore, a considerable proportion of chlorine, which is, of course, absent from the "brown (black) substitutes"; thus it is possible easily to distinguish by chemical means between the two classes of rubber substitutes.

The white substitutes form a yellowish, elastic, crumbly substance of oily smell and neutral reaction; the brown (black) substitutes occur in commerce either as sticky lumps or as a coarsely ground powder.

To manufacture the white substitutes a suitable oil, especially rape oil, castor oil, soya bean oil,[1] maize (corn) oil, sesamé or arachis oil,[2] is dissolved in carbon tetrachloride, in a wooden, or earthenware, or enamelled iron vessel. Whilst the oil is agitated, sulphur chloride is run in,[3] the agitation being continued until the mass has solidified. The reaction is accompanied by evolution of hydrochloric acid gas.[4]

---

[1] *Journ. Soc. Chem. Ind.*, 1894, 1020.

[2] French patents 11,814; 393,868.

The brown substitutes are manufactured by heating oils with sulphur to 160° C. In the United States considerable quantities of brown substitutes are made from maize (corn) oil by heating 50 parts of oil to 470° F. and mixing with it about 20 parts of molten sulphur.

The nature of the chemical change which takes place is not yet fully understood, and little can be added to the notes given (Vol. I. Chap. VII.) under the head of sulphur chloride.[5] *Henriques* has shown that blown oils require much less sulphur chloride than do the original oils to form vulcanised oils; this seems to favour the opinion that the white substitutes are addition products. On saponification, the chlorine only is eliminated (as hydrochloric acid), the sulphur remaining in chemical union with the oils, so that unsaturated substances are again obtained, as is proved by the high iodine numbers of the sulphurised fatty compounds. The sulphur cannot be present in the form of an SH group, as the acetyl values of the substitutes are low. Nor is the action of sulphur on oils fully understood. Whereas melted sulphur does not interact with a saturated fatty acid, such as stearic acid, at about 130° C., oleic acid [6] readily absorbs ten per cent of sulphur at 130°-150° C. The sulphur does not crystallise out on cooling; nor is sulphuretted hydrogen evolved. The reaction which takes place appears therefore to consist of a true addition. It differs most essentially from the action of sulphur on oils at higher temperatures, for even stearic acid is attacked by sulphur at 200° C. with evolution of sulphuretted hydrogen, much as oleic acid heated with sulphur to 200°-300° C. is converted into sulpho-oleic acid with concomitant formation of sulphuretted hydrogen (cp. Vol. I. Chaps. I. and III.).

Altschul states that all oils behave in the same manner, viz. form addition compounds with sulphur, which on saponification yield salts of sulphurised fatty acids; the latter are obtained in their free state on decomposing the soaps with a mineral acid.

Henriques [7] proved, however, that the reaction is not so simple, and that addition and substitution take place concurrently, the former preponderating at low temperatures, the latter at high ones. Also *Michael* [8] showed that the action of sulphur on unsaturated organic compounds is of a complicated nature.

Whether or no the vulcanised oils are thiozonides is not proved.

---

[1] Gössel and Sauer, German patent 228,887; Erdmann, *Liebig's Annal.*, 1908 (362), 171.

[2] Linseed oil and cotton seed oil are less suitable.

[3] Höhn (*Chem. Revue*, 1900, 113) states that in the case of colza oil not less than 17 per cent of sulphur chloride must be used.

[4] An automatic apparatus for this manufacture has been patented by N. Reif, French patent 397,412; German patent 222,140; also W. Spielter, German patent 216,782.

[5] *Bysow. Kolloid Zeits.*, 1910, 281.

[6] Altschul, *Journ. Soc. Chem. Ind.*, 1896, 282.

[7] *Journ. Soc. Chem. Ind.*, 1896, 282.

[8] *Berichte*, 1895, 1633.

Reasoning by analogy and in view of the work of *Erdmann*, it would appear likely that thiozonides are formed.

Oxidised oils have also been proposed for the manufacture of vulcanised oil, and the advantage has been claimed for them (see above) that they require less sulphur or sulphur chloride than do the original oils. It is doubtful whether the vulcanised oils prepared from oxidised oils are preferable to the ordinary vulcanised oils.

The preparation of an india-rubber substitute by heating a solution of amber-resin in castor oil to 180° C. with a small proportion of sulphur treating the sulphurised product, after cooling, with ozonised air, and then with sulphur chloride in the presence of a solvent at a low temperature, has been patented by *Tiehsen.*[1]

The preparation of sulphurised compounds of fatty acids and of their esters will be described under "Fatty Acids." The production of rubber substitutes from the metallic salts or the glycerides of naphthenic acids in admixture with vulcanised oils has been patented by *Chercheffsky.*[2] The addition of naphthalene to the oil before vulcanisation or of a compound of naphthalene and sulphur has been proposed for the manufacture of rubber substitutes.[3]

The "quantitative reactions" naturally lend themselves as suitable methods in the examination of india-rubber substitutes. They must be supplemented, of course, by such tests as the nature of the substance requires.[4]

It should be noted that the saponification of the sulphurised oil must be carried out in the cold in order to avoid loss of sulphur.[5] In this case *Henriques*' method of cold saponification described above (Vol. I. Chap. II.) will be found suitable.

The content of sulphur is estimated by treating the substitute with fuming nitric acid in the presence of silver nitrate, and subsequently fusing with caustic potash and potassium nitrate. The insoluble silver compounds contain all the chlorine.[6]

The following table reproduces some analyses of india-rubber substitutes by *Henriques* :—

---

[1] English patent 17,579, 1904; German patent 160,120 (Spatz and Tiehsen).

[2] German patent 228,858.

[3] English patent 16,971, 1908; French patent 292,669; German patent 224,040.

[4] *Journ. Soc. Chem. Ind.*, 1894, 47, 70.

[5] For whilst the chlorine is eliminated by the alcoholic soda, the sulphur remains in the molecule.

[6] Cp. also Frank and Markwald, *Gummi Zeit.*, 1908 (22), No. 50. Spence and Scott, *Zeits. f. Kolloide*, 1910 (8), 304; 1911 (9), 300; Dr. K. Loewen, *Zeits. f. angew. Chem.*, 1912, 1610.

Oils vulcanised with S_2Cl_2.	Sulphur.	Chlorine.	Water.	Residue on Ignition.	Fatty Acids.	Iodine Value.	Acetyl Value.	Fatty Acids.		
								Sulphur.	Chlorine.	Iodine Value.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		Per cent.	Per cent.	
Linseed oil rubber substitute from raw oil	9·34	8·84	3·02	...	79·6	56·3	21·0	9·88	Trace	160·3
Linseed oil ,, ,, ,, blown oil	4·78	4·85	0·85	...	81·67	52·6	19·6	4·06	0·60	141·2 121·0
Rape oil ,, ,, ,, commercial oil	8·28	7·62	...	...	86·89	32·5	31·0	8·34	Trace	101·5
Rape oil ,, ,, ,, blown oil	6·59	5·95	...	...	87·95	26·9	...	6·54	Trace	102·8
Poppy seed oil ,, ,, ,, blown oil	7·68	7·44	...	...	74·90	33·6	...	8·32	...	133·3
Cotton seed oil ,, ,, ,, blown oil	6·23	5·36	...	...	...	30·3	51·3	6·44	Trace	91·5
Castor oil ,, with minimum of sulphur chloride	4·82	6·70	...	...	85·35	35·2	...	5·32	Trace	136·2 147·4 152·1
Castor oil ,, ,, maximum ,, ,,	10·60	8·95	...	...	...	21·9	105·6	...	0·26	105·6
Commercial Products.										
White substitute, No. 1	6·4	5·0	0·85	0·8	90·45	30·9	...	6·12	0·83	91·3
,, ,, No. 2	6·17	5·86	1·0	5·51	73·58	31·0	...	6·45	0·43	91·2
,, ,, No. 3	8·25	8·88	...	...	...	32·6	...	8·15	...	102·3
Brown substitute, No. 1	15·48	0·7	...	...	...	42·0	...	14·14	...	129·0
,, ,, No. 2	17·71	0·36	...	...	...	42·0	...	15·20	...	125·6

Tung oil[1] and also fish oils have been subjected to the same treatment on a large scale, but hitherto the products so obtained have not found practical application. The material prepared by saturating fibrous material with fish oils, and subjecting the mass to treatment with sulphur chloride, was known under the fancy name "volenite."[2] The chlorides of selenium and tellurium simulate sulphur chloride in their action on oils and fats. Their use in the preparation of rubber substitutes has been patented by *Klopstock*.[3]

Claim has been made for the application of india-rubber substitutes in the manufacture of dynamite as an absorbent (in the place of kieselguhr).[4] For rubber substitutes prepared from "nitrated oils" see below.

VII.—NITRATED OILS

French—*Huiles nitrées.* German—*Nitrierte Öle.*

On treating linseed oil or castor oil with a nitrating mixture, such as is employed in the manufacture of nitroglycerin—two parts (by weight) of concentrated sulphuric acid, 1·845, and one part of nitric acid, specific gravity 1·5—"nitrated" oils are obtained.[5] The nitrated oils are viscid liquids, heavier than water; thus the product obtained from linseed oil has the specific gravity 1·112, that from castor oil 1·127. The nitrated castor oil is insoluble in carbon bisulphide. The composition of these substances is not yet known. They contain 4 to 5 per cent of nitrogen. Samples examined by the author had high saponification values, varying from 278·5 to 286·5. *F. Gehre*[6] saponifies the glycerides with sulphuric acid and washes them before nitrating the resulting mass.

The most prominent property of these products is that of forming homogeneous compounds with nitro-cellulose. Thus a mixture of one part of nitrated castor oil with nine parts of nitro-cellulose yields a product resembling ebonite.

Solutions of these compounds in acetone are used as varnishes, as a basis for paint, and for enamelling leather.

By heating "nitrated oils" to 130° C., or by oxidising them with lead peroxide, rubber-like substances are obtained.[7]

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[1] A salve-like substance obtained by heating tung oil with 0·5-10 per cent of sulphur until a clear solution results, is patented by Alexander, German patent 137,340.

[2] Cp. also Scammell and Muskett, English patent 21,229, 1901; French patent 319,074; and United States patent 724,618.

[3] German patent 260,916.

[4] German patent 110,621.

[5] W. F. Reid, *Journ. Soc. Chem. Ind.*, 1899, 972. Reid and Earle, English patent 21,995, 1895; Velvril Company, German patent 103,726. The nitration of tung oil has been patented by G. Howse, English patent 152,095, 1919.

[6] French patent 398,748.

[7] Velvril Company, Limited, and Howkins, English patent 13,306, 1903; German patent 168,359. Cp. also English patent 27,202, 1903.

VIII.—SULPHONATED OILS, TURKEY-RED OILS[1]

French—*Huiles sulfonées, huiles pour rouges turc.* German—*Sulphonierte Öle, Türkischrotöle.* Italian—*Olii sulfonici, olii per rosso turco.*

The action of concentrated sulphuric acid on oils and fats has been explained already (Vol. I. Chap. I.). This reaction has been employed since 1877 on a large scale in the manufacture of Turkey-red oils.

Turkey-red oil is a fatty substance used in the preparation of the cotton fibre for dyeing and printing Turkey-red. The part which the Turkey-red oil plays is not fully understood yet; opinions differ as to whether it exercises a physical or a chemical action. The advocates of the former explanation assume that the oil protects the lake formed on the fibre, much as boiled linseed oil serves to protect a painted surface. The supporters of the chemical theory hold that the Turkey-red oil combines with alumina and finally with the colouring matter to form a compound lake. In those cases, however, where chemical combination with formation of a lake is excluded on account of the chemical constitution of the colouring matter, the physical theory appears to commend itself. Thus the Turkey-red oil is not a mordant proper, but acts as a fixing agent in so far as it imparts to the dyed fabric a better and superior lustre, which does not belong to the unoiled fibre. The sulphonated oils would appear to the author to be absorbed by the fibre in the same manner as glycerin (from soft soaps) is fixed on the fibre.

Before the process of sulphonating castor oil was discovered (1875), rancid olive oil (see Vol. II. "Olive Oil") and sulpholeates (see p. 210) and sulphonated oils (see p. 210) were used as a Turkey-red oil (*Runge*). At present Turkey-red oil is prepared by allowing concentrated sulphuric acid to run into *castor oil* slowly with constant stirring, taking care that the temperature of 35° C. is not exceeded.[2] If necessary, the mass must be cooled, for secondary reactions take place at temperatures above 35° C. with liberation of sulphurous acid. The product is then mixed with a small quantity of water and the dilute acid allowed to settle out. The lower layer is drawn off[3] and the oil washed with a solution of *Glauber's* salt, until the washings are only slightly acid. Finally ammonia is added, until a sample gives a clear solution with a small quantity of water. Some manufacturers use soda instead of ammonia, or a mixture of ammonia and soda.[1] Since the sulphonated oil is not completely neutralised by alkali, the resultant product still possesses a strong acid reaction.

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[1] Fremy, *Ann. de Chim. et de Phys.*, 1831, 65, 121; *Annalen*, 19, 296; 20, 50. Lightfoot, English patent 769, 1864. Müller-Jacobs, *Journ. Soc. Chem. Ind.*, 1884, 257; 412. 1885, 18; 21; 115. Liechti and Suida, *Journ. Soc. Chem. Ind.*, 1886, 662; *Dingl. Polyt. Journ.* 250, 543; 251, 171; 254, 350; *Berichte*, 1883, 2453. H. Schmid, *Dingl. Polyt. Journ.*, 254, 346. Sabanejeff, *Berichte*, 1886 (19), Ref. 239. M. and A. Saytzeff, *Berichte*, 1886 (19), Ref. 541. Benedikt and Ulzer, *Journ. Soc. Chem. Ind.*, 1887, 543; 1888, 328. Geitel, *Journ. f. prakt. Chem.*, 1888, 53. Löchtin, *Journ. Soc. Chem. Ind.*, 1890, 498. Scheurer-Kestner, *Journ. Soc. Chem. Ind.*, 1891, 471, 555. Wilson, *Journ. Soc. Chem. Ind.*, 1891, 26; 1892, 495. Juillard, *Journ. Soc. Chem. Ind.*, 1892, 335; 1893, 528; 1894, 820. Wolff, *Chem. Revue*, 1897, 103; Herbig, *Färber Zeitung*, 1902, 277; 1904, 21, 38. *Zeits. f. Farbenindustrie*, 1907, 169; 185. v. Neiderhausen, *Bull. Soc. Ind.*, Mulhouse, 1902, 72, 389. Erban and Mebus, *Zeits. f. Farbenindustrie*, 1907, 169, 185; 1908, 312, 317. *Zeits. f. angew. Chem.*, 1909, 55; Woldenberg, *Inaug. Dissert.*, Zurich, 1908.

[2] A process has been patented for preparing a product by sulphonating in the presence of aldehyde and acetine, both of which are stated to act as condensing agents.

[3] Any glycerin that has been set free is contained in this layer. Cp. French patent 349,380.

Turkey-red oil containing a higher percentage of sulphonic esters is obtained by replacing the sulphuric acid by chloro-sulphonic acid.[2]

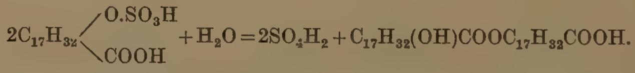
The sulphonated oil, as obtained by the treatment with concentrated sulphuric acid, can be resolved into two portions by dissolving it in ether, washing with brine until it is free from sulphuric acid, and then shaking out repeatedly with water. On treating the united aqueous solutions with sodium chloride the *water-soluble portion* separates as an oily layer. On evaporating off the ether from the ethereal solution the *water-insoluble portion* is obtained.

Benedikt and Ulzer stated that the *water-soluble portion*, in the case of a Turkey-red oil prepared from castor oil, consists of *ricinoleo-sulphuric acid* (see Vol. I. Chap. III. " Ricinoleic Acid ").

This acid is miscible with water in all proportions ; the aqueous solutions lather like ordinary soap solutions. From these solutions the ricinoleo-sulphuric acid is precipitated as a heavy oily layer by brine, moderately dilute sulphuric acid, or hydrochloric acid.

By adding salts of calcium, barium, aluminium,[3] lead, copper, etc., to the solution of the acid, viscous precipitates are obtained. On boiling the aqueous or alkaline solutions of ricinoleo-sulphuric acid, the acidic portion remains intact. If, however, the free acid be boiled with dilute hydrochloric or sulphuric acid, part of it is decomposed into ricinoleic and sulphuric acids, whilst another part is converted into a ricinoleic anhydride.

Indeed *Grün and Wetterkamp*[4] state that neither is sulphurous acid liberated nor is a dihydroxylated acid formed, the reaction that does take place resulting in the splitting off of sulphuric acid and in the formation of an inner anhydride, as is expressed by the following equation :—



$$2C_{17}H_{32}\left\langle\begin{matrix}O.SO_3H\\COOH\end{matrix}\right. + H_2O = 2SO_4H_2 + C_{17}H_{32}(OH)COOC_{17}H_{32}COOH.$$

The acid value of the product obtained is approximately 92 ; as the theoretical number is 97·6, this would prove that small quantities of other anhydrides are formed.

On boiling ricinoleo-sulphuric acid with water in the presence of a mineral acid, the decomposition is considerably accelerated, and the formation of esters proceeds beyond the stage indicated by the preceding equation ; probably a lactide of the following composition is formed :—

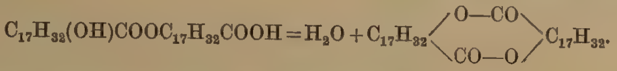
---

[1] The first Turkey-red oil discovered by *Writh* in Ramsbottom that came into the market was prepared with soda. Very shortly after that a Turkey-red oil, prepared with ammonia, was prepared by F. E. Storch.

[2] Grün, German patent 260,748.

[3] It may be mentioned here that Scheurer (*Journ. Soc. Chem. Ind.*, 1893, 1025) proposed metallic sulpholeates—aluminium sulpholeate especially—as mordants for steam colours.

[4] *Zeits. f. Farbenindustrie*, 1908, 375.



$$C_{17}H_{32}(OH)COOC_{17}H_{32}COOH = H_2O + C_{17}H_{32}\left\langle\begin{matrix}O—CO\\CO—O\end{matrix}\right\rangle C_{17}H_{32}.$$

Wagner[1] withdraws his previous statements.

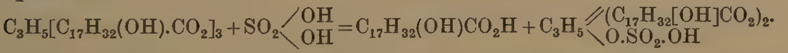
The *water-insoluble* portion of castor Turkey-red oil consists chiefly of free ricinoleic acid and small quantities of neutral (unacted on) oil, and also of anhydrides of ricinoleic acid (cp. however, *Bogajewsky*, below).

Scheurer-Kestner is of the opinion that castor Turkey-red oil consists of a mixture of ricinoleo-sulphuric acid, and of monoricinoleic and diricinoleic acids, the occurrence of the last-named two acids being due to polymerisation of free ricinoleic acid.

According to *Juillard*, polymerisation proceeds further, giving rise to the formation of di-, tri-, tetra-, and penta-ricinoleic acids, an opinion at variance with the views of *Scheurer-Kestner*, who maintains that polymerisation extending beyond the formation of the di-acid is due to a secondary action of hydrochloric acid, liberated on washing the product with brine instead of *Glauber's* salt. In *Juillard's* opinion castor Turkey-red oil is a mixture of varying proportions of poly-ricinoleic acids, of alkali salts of mono- and poly-ricinoleo-sulphuric acids, of anhydrides of the latter acids, and of their products of decomposition[2] (cp. also Vol. I. " Ricinoleic Acid "). This view is supported by the experiments of *L. Radcliffe and S. Medofski*,[3] and also by *M. T. Schilikin*.[4]

Bogajewsky[5] is of the opinion that the action of concentrated sulphuric acid ($\frac{1}{2}$ to 3 parts of SO_4H_2) on castor oil takes place in the following three stages :—

(1) Free ricinoleic acid is formed according to the following equation :—



$$C_3H_5[C_{17}H_{32}(OH).CO_2]_3 + SO_2\left\langle\begin{matrix}OH\\OH\end{matrix}\right. = C_{17}H_{32}(OH)CO_2H + C_3H_5\left\langle\begin{matrix}(C_{17}H_{32}[OH]CO_2)_2.\\O.SO_2.OH\end{matrix}\right.$$

The products of the interaction are completely saponified by half-normal alcoholic potash.

(2) The products formed in the second stage can no longer be completely saponified by means of half-normal alcoholic potash ; the acid number of the product is decreased, in consequence of the sulpho-groups exchanging places with the hydrogen of the hydroxyl-groups, thus—

$$\begin{aligned}&(C_{17}H_{32}[OH]CO_2)_2C_3H_5(O.SO_2.OH) + SO_4H_2\\&\qquad(C_{17}H_{32}.[OSO_2OH]CO_2)_2C_3H_5.OH + H_2O.\end{aligned}$$

In aqueous solution partial dissociation takes place on standing ; in alcoholic solution partial esterification occurs.

The dissociation in the one case and the esterification in the other increase as the proportion of sulphuric acid and the temperature rise.

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[1] *Zeits. f. Farbenindustrie*, 1908, 378.

[2] *Journ. Soc. Chem. Ind.*, 1894, 820.

[3] *Journ. Soc. Dyers and Col.*, 1918, 34, 22.

[4] *Färber Zeit.*, 1914, 25, 419.

[5] *Chem. Zentralbl.*, 1897, ii. 335.

(3) In the third stage the acid value decreases whilst the saponification value increases, the poly-ricinoleic compounds described by *Juillard* being formed.

On treating the product obtained in the second phase with 30 to 50 parts of water, the acid value increases to a maximum and then falls again ; the maximum occurs when two hydroxyl groups have become free. On boiling, the triglyceride is almost completely hydrolysed, with formation of ricinoleic and sulphuric acids.

In the manufacture of the normal commercial Turkey-red oil the interaction of acid and oil is interrupted before the second stage has reached completion. The commercial product contains, therefore, chiefly the following substances :—(*a*) in the *water-soluble* portion, ammonia (or soda) salts of the acids—$(HO . SO_2 . OC_{17}H_{32} . CO_2)$ $(HO . C_{17}H_{32} . CO_2) . C_3H_5 . (OH)$, and $HO . C_{17}H_{32} . CO_2H$; (*b*) in the *ether-soluble* portion, unchanged castor oil and salts of the mixed castor oil fatty acids.

Besides castor oil, other fatty oils (such as olive oil, arachis oil, cotton seed oil, etc.) have been, and still are, used for the production of Turkey-red oils. *L. Radcliffe and C. Palmer* [1] have investigated the changes undergone by the fatty acids when cod oil is sulphonated and find that there is a considerable increase in the mean molecular weight. The yield of ether insoluble bromides had decreased from 42 per cent to 11 per cent.

Benedikt expressed the view that castor Turkey-red oil cannot be replaced by the oils named, because by treating them with sulphuric acid saturated hydroxylated acids and their sulphuric esters are formed, whereas castor Turkey-red oil still consists of *unsaturated* fatty acids. *Benedikt*, therefore, ascribed the superior effect of castor oil to the oxidisability of the castor Turkey-red oil fatty acids.

This statement has, however, not been supported by experiments. Its correctness is doubtful in view of the fact that the castor oil fatty acids are not readily oxidised by blowing (cp. Vol. II. Chap. XIV. "Castor Oil"), and also from the fact that sulphonated oils of great emulsifying powers have been prepared from hydrogenated oils.[2] Sulpholeates first mentioned by *Runge* [3] seemed to have been well known in Yorkshire ; they were prepared according to a process patented by *H. W. Kipley* (1850), and under the name of sulphated oils were prepared in 1847 by *Mercer and Greenwood*. *Schmitz and Tönges* [4] have prepared a "Turkey-red oil" by mixing oleic acid with sulphuric acid and heating the product to 105°-120° C. According to statements of *Werner* [5] this oil is, in certain cases, superior to castor Turkey-red oil.[6]

The preparation of Turkey-red oils from castor oil fatty acids has been proposed by *F. Erban*.[7]

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[1] *Journ. Soc. Chem. Ind.*, 1915, 643.

[2] J. Levinstein and Levinstein, Ltd., English patent 16,890, 1914.

[3] *Farbenchemie*, 1834 (1), 213.

[4] *Journ. Soc. Chem. Ind.*, 1892, 827, German patents 60,579 and 64,073.

[5] *Ibid.*, 1893, 40.

[6] Cp. also Herbig, *Färber Zeitung*, 1902, 277 ; 1904, 24, 38.

[7] *Zeits. angew. Chem.*, 1915, 28, 515.

The chemistry of Turkey-red oils still requires further elucidation by experiments. Evidently reactions similar to those taking place in the "acid saponification process" (cp. Vol. I. Chap. II.; cp. also below) occur. It may be added that *Geitel* (Vol. I. Chap. III. "Oleic Acid") has proved the presence of stearolactone and of the anhydride of the ordinary hydroxy-stearic acid in Turkey-red oil prepared from oleic acid.

The commercial Turkey-red oils are viscous, transparent fluids.

Since the chemical composition of a Turkey-red oil depends on the mode of manufacture, on the amount of sulphuric acid employed, and on the raw material used, the commercial products vary in their composition.

The commercial examination of a Turkey-red oil divides itself into two parts, viz. (1) the practical examination, and (2) the chemical examination. For a biological method of examining Turkey-red oils cp. *R. Kobert and W. Greuel.*[1]

(1) *Practical Examination.*—The sample should give a complete emulsion with ten volumes of water. In practice the test is performed by first mixing, in a graduated cylinder, one measure of oil with a little warm water (with which the oil forms a clear solution). Then water is added gradually until ten measures have been introduced. The appearance of the sample is then compared side by side with an emulsion prepared with a sample of known purity in exactly the same manner. No oily drops should separate after standing for a short time. An adulterated product may be recognised at this stage by not giving a clear solution with a small quantity of hot water, as also by a darker coloration than that observed in the case of a pure oil. The emulsions should show a slightly acid reaction to litmus paper. In case the emulsion be neutral or alkaline, acetic acid is added, drop by drop, until both samples show approximately the same acidity.

The most important test consists in dyeing cotton prepared with the oil. The sample dyeing is carried out in the following manner:—Two pieces of cotton of equal size are treated with the sample and with a standard oil, respectively, by allowing them to soak in an emulsion prepared from 1 part of oil and 15-20 parts of water. After drying, the fabric is mordanted with alum and dyed in alizarin, or paranitro-aniline red is printed on. The samples are then brightened by soaping and finished in the usual manner. The practical test will only be resorted to by a works chemist, or by an analyst who has special experience in that branch of work.

(2) *Chemical Examination.*—Turkey-red oil is valued on the amount of **total fatty matter** in the sample. This comprises the *water-insoluble portion* obtained on adding a mineral acid to the oil (whereby fatty acids, hydroxy acids, and neutral oil are separated), as also the hydroxylated acids obtained on decomposing the soluble sulphuric esters of the fatty acids.

The **total fatty matter** may be determined by *Benedikt's* method.[2]

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[1] *Collegium*, 1916, 261, 305.

[2] *Zeits. f. angew. Chem.*, 1887, 325.

About 4 grms. of the sample are weighed off accurately in a porcelain basin, and 20 c.c. of hot water are added gradually ; should the liquid be turbid, ammonia is run in until the solution is slightly alkaline to phenolphthalein. A clear solution will thus be obtained. 15 c.c. of dilute sulphuric acid, prepared from equal measures of concentrated sulphuric acid and water, are next run in, and an accurately weighed quantity of bees-wax or stearic acid,[1] about 10 grms., is added. The mixture is heated until a clear fatty layer has separated on the top. After cooling, the solidified cake is treated in the same manner as that described under " Soap Analysis " and is then weighed.

The following rapid process, due to *Finsler*, and recommended by *Breinl*,[2] is largely employed in continental practice :—30 grms. of the sample are weighed off accurately, rinsed with about 70 c.c. of hot water into a 200-c.c. flask, the neck of which is graduated in $\frac{1}{5}$ or $\frac{1}{10}$ c.c., 25 c.c. of sulphuric acid of specific gravity 1·563 (52° Bé.) are added, and the mixture is heated to boiling with frequent shaking until the fatty matter forms a clear, transparent layer. A hot concentrated solution of common salt, or *Glauber's* salt, is next added carefully to bring the separated layer of fat into the neck of the flask. After half an hour's standing the volume of fatty matter is read off ; the number of c.c. multiplied by 3·33 corresponds to the total fatty matter expressed in per cents. Since, however, the specific gravity of the fatty matter is below 1 (usually 0·945), a correction should be made.

The total fatty matter thus found is less than the sulphonated oil dissolved in the water by the amount of sulphuric acid split off on boiling with hydrochloric acid.

In addition to the total fatty matter the amount of (*a*) **neutral oil,** (*b*) **sulphonated fatty acids,** (*c*) **ammonia** or **caustic soda,** (*d*) **sulphuric acid,** and (*e*) **water** may be estimated.

(*a*) **Neutral Fat.**—30 grms. of the sample are dissolved in 50 c.c. of water ; 20 c.c. of ammonia and 30 c.c. of glycerin are added, and the mixture is exhausted twice with ether, using 100 c.c. for each extraction. The ethereal solution is then washed with water to remove small quantities of dissolved soap, and the ether is evaporated off. The residue is transferred to a small tared beaker, dried at first on the water-bath, then at 100° C., and weighed. Another method due to *Herbig* [3] is to convert the free acids into the sodium salts, evaporate off the water, and extract the residue with acetone at 0° C. The sodium salts of ricinoleic and sulpho-ricinoleic acids are stated to be very sparingly soluble in this menstruum.

(*b*) **Sulphonated Fatty Acids.**—4 grms. of the sample are boiled in an *Erlenmeyer* flask with 30 c.c. of dilute hydrochloric acid (1 : 5) for 40 minutes, with frequent shaking.[4] After cooling, the liquid is transferred to a separating funnel, and shaken out with ether to extract the fatty matter. The aqueous layer is drawn off and the ethereal layer washed with water. The washings are united with the main aqueous portion and the sulphuric acid determined by precipitation with barium chloride. From the amount thus found the quantity of sulphuric acid, as determined under (*d*) (see below), is subtracted and the difference calculated to sulpho-ricinoleic acid (80 parts of SO_3 correspond to 378 parts of ricinoleo-sulphuric acid $C_{18}H_{33}O_2 . O . SO_3H$). The combined sulphuric anhydride may be determined by the volumetric method due to *R. Hart*.[1] In the first place, a weighed quantity of the oil is titrated with half normal sulphuric acid and the alkalinity expressed in milligrams of KOH per grm. A further portion is boiled with a measured quantity of normal sulphuric acid until the sulphonated oil is completely hydrolysed. The sulphuric acid is then titrated back, using methylorange as indicator. From the difference between the two titrations, which equals the difference between the total alkalinity and the acidity due to the sodium bisulphate formed in the reaction, the amount of combined SO_3 is derived. The decomposition of the sulphonated oil on boiling with sulphuric acid takes place according to the following equation :—

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[1] The stearic acid should not lose weight on heating to 100° C.

[2] *Journ. Soc. Chem. Ind.*, 1889, 573.

[3] *Färber Zeit.*, 1914, 169.

[4] Cp. Herbig, *Chem. Revue*, 1902, 5.

$$2C_{17}H_{32}OSO_3NaCO_2Na + H_2SO_4 + 2H_2O = Na_2SO_4 + 2NaHSO_4 + 2C_{17}H_{32}OHCOOH.$$

(*c*) **Ammonia or Caustic Soda.**—7 to 10 grms. of the sample are dissolved in a little ether, and shaken four times with dilute sulphuric acid (1 : 6), using 5 c.c. each time.

To determine ammonia, the acid liquid is distilled with caustic potash in the well-known manner, and the ammonia received in an accurately measured quantity of standard acid.

To estimate caustic soda the acid liquid is concentrated in a platinum dish on the water-bath, and the excess of sulphuric acid driven off by heating on the sand-bath ; the residue is mixed with ammonium sulphate, ignited, and the sodium sulphate weighed.

(*d*) **Sulphuric Acid.**—The quantity of sulphuric acid present in the form of ammonium or sodium sulphate is found by dissolving a weighed quantity of the sample in ether and shaking it several times with a few c.c. of concentrated brine, free from sulphate. The several washings are united, diluted, filtered, and the filtrate precipitated with barium chloride.[2]

(*e*) **Water.**—The amount of water is usually found by difference, but may be determined direct according to the method of the American Leather Chemists' Association by distilling 30 to 40 grms. of the oil with 75 c.c. of xylene previously saturated with water, from an oil-bath. The distillate is collected in a graduated tube.[3]

The method for the detection of **iron** in Turkey-red oils has been described in Vol. I. Chap. IV.

In view of the many attempts that are being made to substitute for castor oil other oils,[4] and in view of the many substitutes that are actually met with in commerce, it is frequently necessary to determine the nature of the oils used in the manufacture of a sample of Turkey-red oil.

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[1] *Journ. Ind. Eng. Chem.*, 1917, 9, 850, and *Journ. Amer. Leather Chem. Assoc.*, 1920, 15, 404. Cp. also G. Bumcke, *ibid.*, 1921, 16, 7, and G. F. Pickering, *Journ. Soc. Chem. Ind.*, 1920, 305 T.

[2] Cp. also E. Kern, *Journ. Ind. and Eng. Chem.*, 1920, 785.

[3] Cp. also G. Bumcke, *Journ. Amer. Leather Chem. Assoc.*, 1915, 10, 559 ; and *Journ. Soc. Leather Trades' Chem.*, 1919, 3, 101.

[4] Erban and Mebus, *Zeits. f. Farbenindustrie*, 1907, 169, 185 ; 1908, 317.

Of the greatest importance in the examination is the determination of the acetyl value. Castor having the highest acetyl value of all oils known will be thus readily identified.

An acetyl value of 125 or above will point to pure castor oil; in case other oils have been used, lower values will be obtained.

A sample of a genuine castor Turkey-red oil examined in the author's laboratory gave the following result:—

	Per cent.
Total fatty matter	40·1 [1]
Unsaponifiable	0·15

The examination of the fatty matter obtained by saponification led to the following numbers:—

Specific gravity at 15° C. . . .	0·9449
Iodine value	82·1
Acid value	174·3
Saponification value	189·3
Acetyl value	126·9

Lane [2] bases another method on the fact, ascertained by him, that lead ricinoleate is practically insoluble in low boiling petroleum ether. *Lane* proceeds as follows:—3 to 3·5 grms. of the "total fatty matter," as obtained above, are saponified with alcoholic potash and converted into lead soap in the manner described in Vol. I. Chap. VIII. The lead soap is boiled out repeatedly, under a reflux condenser, with low boiling petroleum ether, and the solutions are poured off into a 500-c.c. flask or cylinder. Altogether 200 to 225 c.c. of petroleum ether are used. The solution is diluted to nearly 500 c.c. with petroleum ether of boiling point 28-30° C., boiled for one minute, cooled, made up to 500 c.c., and allowed to stand overnight in a cool place, when the insoluble lead ricinoleate settles out completely. 250 c.c. of the solution are drawn off (or filtered off if necessary), distilled down to 75-80 c.c., and decomposed with 10 c.c. of 10 per cent acetic acid in a separating funnel. The solution of fatty acids in the petroleum ether is washed with water until the washings are neutral. The petroleum ether is evaporated off and the residue dissolved in 50 c.c. of neutralised alcohol and titrated with decinormal soda. The alkali is calculated to oleic acid; the percentage divided by 80 is said to give the amount of oils other than castor oil. The quantity of castor oil is found by difference. The factor 80 is chosen as most of the oils used as castor oil substitutes contain about 80 per cent of liquid acids. If the admixed oil can be identified, its true percentage of liquid acid should be substituted for 80.

The accuracy obtainable by this method may be illustrated by *Lane's* results, reproduced in the following table:—

---

[1] The highest-priced Turkey-red oils contain about 50 per cent of total fatty matter. It should be noted that some manufacturers refer the guaranteed percentages (35, 40, 50) to the amount of "sulphonated fatty acids."

[2] *Journ. Soc. Chem. Ind.*, 1907, 597.

Used.	Castor Oil found.
Castor oil, 50 parts ; olive oil, 50 parts	47·83 per cent
,, ,, 70 ,, ; ,, ,, 30 ,,	69·96 ,, ,,
,, ,, 85 ,, ; ,, ,, 15 ,,	84·57 ,, ,,
,, ,, 85 ,, ; ,, ,, 15 ,,	84·45 ,, ,,

The defect inherent to Turkey-red oils prepared as described above, namely, that of giving rise to the formation of insoluble lime and magnesia soaps with hard water, is obviated—at any rate to some extent—by introducing some modifications of the usual process.

A product of this kind is the sulpho-ricinoleate obtained by neutralising the product of the reaction of sulphuric acid on castor oil with an alkali, without washing out the free sulphuric acid.[1] Hence this soap (" sulpholeate of sodium ") contains considerable quantities of sodium sulphate, and is much richer in fatty matter than the Turkey-red oils prepared by the process described above (p. 207). Another class of oils of this kind are those which represent a mixture of hydroxy acids (" oxyoleates ") with sulphonated castor oil.[2] They are prepared by sulphonating castor oil or other oils, or oleic acid, etc., with sulphuric acid in the usual manner and boiling the washed product with water in an open vessel, until the sulpho-compounds are decomposed with formation of hydroxy acids (just as the total fatty matter is prepared for the chemical examination). These hydroxy acids are then mixed in various proportions with castor oil, and the mixture is heated from 40° to 100° C. The mixture is then allowed to cool, and sulphonated with sulphuric acid in the same manner as in the manufacture of ordinary Turkey-red oil. The product is then washed free from sulphuric acid and treated with alkali until a water-soluble oil is obtained.

It is difficult to understand what effect the heating from 40° to 100° C. is intended to produce. The inventor seems to have felt this himself, and in a further patent[3] he claims as an improvement the omission of the heating in the above-described process. The production of Turkey-red oil by sulphonating the petroleum acids (naphthenic acids) has been patented by *Petroff*.[4]

The well-known cleansing properties of Turkey-red oil have led to its application for the lubricating and cleansing of wool (see above, p. 103), as also to its use as a base for emulsified oils (p. 116) and textile soaps (see below, " Textile Soaps ").

The use of sulphonated fatty acids as a degreasing agent and for removing lime alumina and magnesium soaps has been patented by *Guétan and Simonin*.[5]

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[1] Stockhausen, German patents 113,433, 126,541, 159,220, 169,930; English patent 21,280, 1908; L. E. Common and Hull Oil Manufacturing Co., English patents 23,768, 1906; 16,969, 1907 (cp. p. 355).

[2] A. Schmitz, French patent 376,555; English patent 8245, 1907.

[3] English patent 11,903, 1907; French patent (first edition to No. 376,555) No. 7908.

[4] German patent 274,786.

[5] French patent 400,105.

C.—INDUSTRIES BASED ON THE SAPONIFICATION OF OILS AND FATS

The important industries which are based on the hydrolysis (saponification) of oils and fats comprise the manufacture of stearine candles, soaps, and glycerin. The scientific principles which underlie the manufacture of these products have been fully discussed from a theoretical point of view in Vol. I. Chap. II. In this section the industries founded on them will be considered from a practical point of view. Whereas the soap industry, like many of the older chemical industries, had reached a high degree of development on exclusively empirical lines, long before its scientific foundation was understood, the manufacture of stearine candles and of glycerin are the direct outcome of the scientific researches of *Chevreul*.

I.—CANDLE INDUSTRY

In this work the chief attention must be paid to the manufacture of stearine candles; other materials used in the candle industry, such as the mineral waxes, can therefore only be considered briefly. The vegetable and animal waxes, which are used as candle material, beeswax, spermaceti, etc., will be dealt with in the section "Technology of Waxes."

STEARINE CANDLES, COMMERCIAL "STEARINE," COMMERCIAL STEARIC ACID

The saponification processes at present employed on a manufacturing scale in the stearine candle industry are as follows:—

(1) Aqueous Saponification.
(2) Saponification with the Assistance of Bases.
(3) Sulphuric Acid Saponification. Acid Saponification.
(4) The Mixed Process.
(5) Saponification by means of Sulpho-compounds.

A preparatory treatment of the fats consists in freeing them from gross impurities by sedimentation or by filtration, or, if need be, by treatment with dilute acids. *Fournier and Co.*[1] claim that a preliminary heating of the fats to 110-120° C. whilst a current of air is blown through for a "sufficiently long time to oxidise energetically" is beneficial for the ready hydrolysis of the fats. This treatment is intended to precede in processes (2) and (3) the "autoclaving" and the "acidification." In the fourth process this treatment is to be applied after the acidified mass has solidified.

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[1] French patent 339,385.

(1) Aqueous Saponification

The realisation of the fundamental equation of fat hydrolysis :—

$$C_3H_5(OR)_3 + 3H.OH = C_3H_5(OH)_3 + 3R.OH$$

suggests itself to the candle-maker as the ideal process. The first attempt to work such a process on an industrial scale was made by *R. A. Tilghmann*,[1] whose method consisted in forcing an emulsion of fat and water through a coiled iron tube heated in a furnace to a temperature of about 330° C. This process was, however, soon abandoned on account of the saponification being incomplete and considerable quantities of fatty matter being destroyed. The efforts of later inventors to carry out the hydrolysis of fats in an autoclave by means of water have met with greater success. From the table "Aqueous Saponification of Neutral Fats under Pressure," Vol. I. Chap. II., it will be gathered that with the increase of the pressure under which the water acts on the glycerides, or in other words, with the increase of temperature of the heating steam, the rate at which hydrolysis takes place is much increased. In practice, steam at a pressure of 15 atmospheres (equalling about 220 lbs. per square inch) and corresponding to a temperature of about 200° C. is capable of effecting hydrolysis.

The apparatus working on a practical scale is shown in Figs. 9 and 10.

Fig. 9 represents *Hughes'*[2] apparatus, which the author saw in operation in a Paris candle-works. The fat is charged into the autoclave A, about 30 per cent of water is added, and steam, generated in a multitubular boiler at a pressure sufficiently high to keep up a working pressure of 15 atmospheres in the apparatus, is sent into the autoclave. The steam is finely divided into streamlets by a distributor similar to the one shown in Fig. 11. In order to provide additional security (against explosion) beyond that afforded by the safety valve, and in order to agitate the mass thoroughly, a small amount of steam is allowed to escape continuously through the pipe E, which thus serves as an extra safety valve. The escaping steam is utilised for the concentration of a glycerin solution charged (through pipe G) into vessel B, in which is enclosed a heating coil connected with E, the condensed water escaping through valve F, which acts as a kind of steam trap. The steam evolved from the glycerin solution in B serves to pre-heat a dilute glycerin solution fed into vessel C at J. In consequence of the high temperature employed, the fatty material becomes seriously discoloured, so that the fatty acids must be chiefly worked up by the "mixed process" (p. 242). Moreover, since the hydrolysis of the fat does not reach so high a percentage as is the case in the processes described under (2), a small proportion of lime, about 1 per cent, is usually added to the mass in the autoclave. Hence, practically speaking, this method approaches very nearly those described under "Aqueous Saponification with the Assistance of Bases."

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[1] English patent 47, 1854; *Berthelot* also showed at this time that glycerides can be hydrolysed by water alone at a temperature of 220° C.

[2] English patent 6562, 1885. Cp. also E. Böhm, German patent 292,496 and English patent 28,840, 1913.

It has been shown (Vol. I. Chap. II.) that saponification is accelerated by intimate contact of the reacting masses. In *Hughes*' autoclave this is obtained, as pointed out already, by a portion of the steam which enters the autoclave under high pressure being allowed to escape continuously. In order to produce a still more intimate intermixture *Michel*[1] designed the apparatus shown in Fig. 10. A pair of autoclaves are worked conjointly. They are charged through the pressure vessel A and pipe *e* with fat and water. The autoclaves are heated by fire, and as the pressure rises their contents are forced up (through the tubes *f*, *f′*, which reach almost to the bottom of the autoclaves) into the top of the mixing vessel C, whence the mass runs back again into the autoclaves.

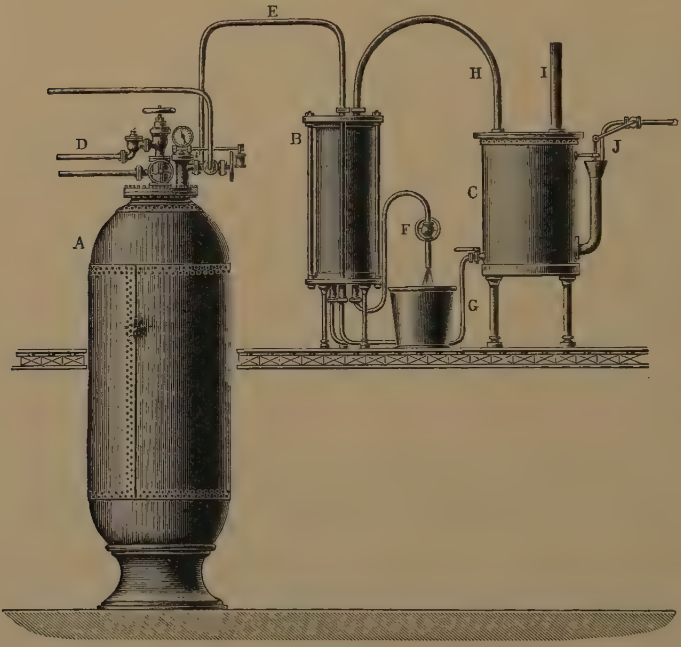

Fig. 9.

Being somewhat cooled in C, it falls to the bottom of the autoclave through the hot mass therein, thus contributing to the thorough intermixing of the fat and water. This play repeats itself whilst the pressure on the autoclaves is kept up at 15 atmospheres for eight hours. The hydrolysed mass is then forced through pipe *h* into the vessel D, in which separation into two layers—an upper layer of fatty acids and a lower layer of glycerin water ("sweet water")—takes place. The heating of the autoclave by direct fire is, however, a serious disadvantage of the process, as this may lead to the burning of the fat. Therefore, *Michel's* method is less acceptable than *Hughes'*. The autoclaves were shown at the Paris Exhibition of 1889, but, as far as the writer is aware, the process has not been adopted in Europe.[1]

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[1] English patent 8403, 1885; *Journ. Soc. Chem. Ind.*, 1886, 432. Cp. also E. Haehl, German patent 51,462, 1889.

Since the pressure and the temperature of steam stand in a definite relation to each other, it follows that high pressure steam may be replaced by superheated steam standing under ordinary pressure. Hence hydrolysis should become feasible by treating fats with superheated steam at a sufficiently high temperature. A process based on the hydrolysis of fats by means of steam under the ordinary pressure was patented as early as the year 1825,[2] but it did not gain practical importance until *Wilson and Payne*[3] took out their patent for "Improvements in distilling fatty and oily matters." In their process glycerides were heated in a still, whilst superheated steam was sent through the fatty mass, the temperature of which was kept between 550° and 600° F. The products of hydrolysis, viz. the fatty acids and glycerol, were carried over by the water vapours. The apparatus employed was similar to the one illustrated in Fig. 19. Although this

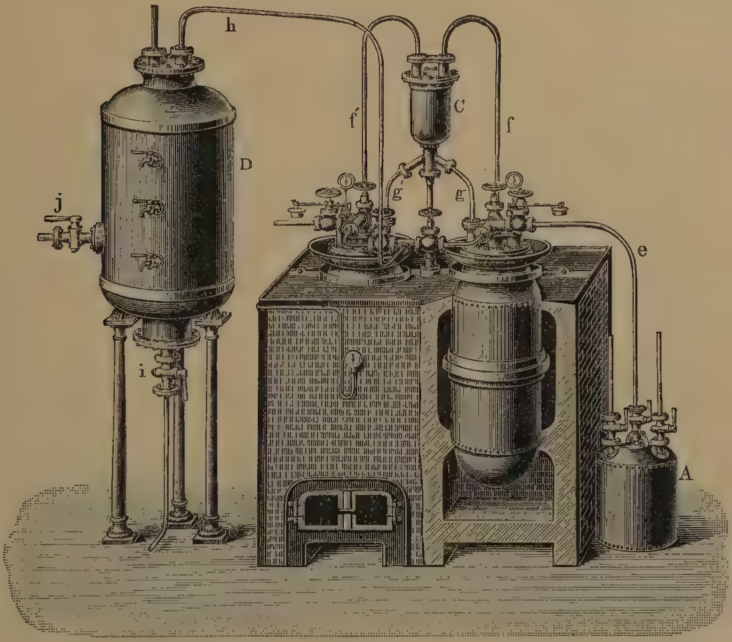

Fig. 10.

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[1] A process of hydrolysing under high pressure with the aid of sulphurous acid has been patented by Budde and Robertson, English patent 5715, 1909.

[2] English patent 5183, 1825.

[3] English patent 1624, 1854. Cp. also Gwynne, English patent 8681, 1840.

process was worked for a number of years it has been abandoned, since considerable quantities of fatty matter underwent destruction.

Lewkowitsch[1] endeavoured to render this mode of hydrolysing practicable by heating the fats in a current of superheated steam *in vacuo*. This process also proved unremunerative, and has therefore been abandoned. Essentially the same process, with the modification that an electric current is sent through the fats or that a galvanic couple is fixed inside the vessel, has been patented.[2] The use of an electrolysed salt solution containing a small amount of free soda has been proposed by *Andrault*.[3]

The products of hydrolysis obtained in *Hughes*' and *Michel's* processes are treated in the same manner as those obtained in the following processes.

(2) Aqueous Saponification with the Assistance of Bases

The chemical equation symbolising the saponification of fats by means of bases has been given in Vol. I. Chap. II. It has also been shown there that in order to effect complete saponification in an *open* vessel, a larger quantity of bases is required than theory demands. Indeed, if lime be used, the proportion of caustic lime—CaO—must be 12-14 per cent instead of the theoretical quantity of 9·7 per cent.

The technical process based on the saponification of oils and fats by means of 12-14 per cent of lime and leading to the conversion of the total fatty acids into lime soaps is due to *de Milly*.[4] The fat is churned up with water in an open lead-lined vat by means of live steam sent into the emulsion through an open coil; whilst the mass is kept in ebullition, caustic lime previously slaked and made into a thin cream is gradually introduced. The boiling is kept up until the saponification is complete; this is readily recognised by the lime soap separating from the water in a curdy form. The glycerin water—" sweet water "—is then run off, the still soft lime soap is washed to remove occluded glycerol, and is then decomposed with sulphuric acid. In the older methods the lime soap was allowed to cool, when it settled as a hard mass—" rock "—from which the supernatant glycerin solution was run off. This hard lime soap was then washed, reduced to powder by grinding, and decomposed with sulphuric acid, when the calcium was precipitated as sulphate, whilst the liberated fatty acids rose to the top as a clear oily layer. The fatty acids and the glycerin " sweet water " are worked up for candle material and crude glycerin, as will be described below.

The large amount of lime (and consequently the large amount of sulphuric acid) required in this process renders it a very costly one, so that it has been largely superseded by methods of saponification under pressure (see below). Still, the simple and inexpensive installation required for the operation, and the ease with which it can be carried out, combined with the fact that the fatty acids so obtained yield the best and purest candle material, have been instrumental in keeping this process alive, especially in *small* works.

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[1] English patent 5985, 1888.

[2] Simpson, French patent 364,587. Harvey and Simpson, English patents 26,917, 1905; 175, 1906. Cp. also Magnier, Bragnier, and Tissier, below, " Conversion of Oleic Acid into Candle Material."

[3] French patent 464,248.

[4] The first patent by de Milly et Motard (1833) claims the saponification by means of lime in a *closed* vessel, the quantity of lime used not being mentioned. The patent of Chevreul and Gay-Lussac (1825) claimed saponification by means of potash and decomposing the soap.

A modification of this method has been worked out during latter years by *Krebitz*.[1] The saponification with lime is in principle the same as described above, with this difference, however, that the fat is not boiled with the lime until separation of the lime soap takes place, but that the lime water is brought into a state of complete emulsion with the oil and fat at a temperature not exceeding 100° C. This emulsion is then allowed to stand overnight, when saponification takes place spontaneously, and a softish mass results which occludes the water introduced with the lime and the glycerol formed. This mass does not offer as much difficulty in grinding as the "rock" does. The ground lime-powder is then washed free from glycerol, when the lime soap is ready for further treatment. *This process is unsuitable for candle-works.* It has been introduced in some small Continental soap-works working up low-class bone fats, where the ground lime soap is converted into soda soap by double decomposition with sodium carbonate solution (see "Soap Manufacture"). The chief advantage of this modification of the lime saponification process lies in the fact that the lime soap contains only a moderate amount of water, is very porous, and therefore suitable for grinding into powder. *C. Ferrier*[2] claims to obtain the same result, enabling the operator to maintain the steam at a temperature below 100° C., by carrying out the saponification in an "autoclave" under a partial vacuum.

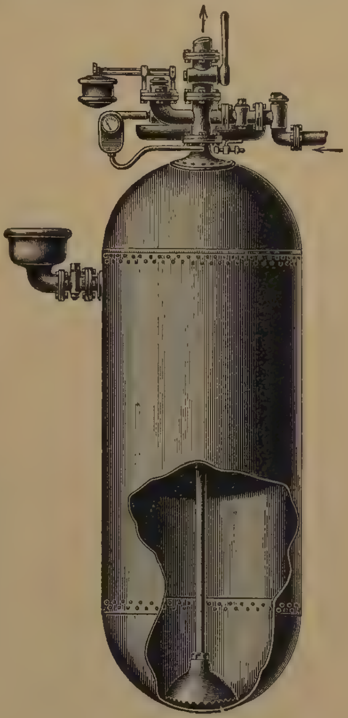
Fig. 11.

In large establishments reasons of economy render a reduction of the proportion of bases and acid imperative. Such reduction is possible through treating the fats with milk of lime in an autoclave under pressure. It has been shown in Vol. I. Chap. II. that as the pressure rises the amount of bases may be reduced, the bases merely acting as accelerators. Hence the greater the pressure the less bases need be used.

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[1] German patent 155,108.

[2] French patent 366,460.

In the modern practice of candle-works autoclaves are therefore worked at a pressure of about eight atmospheres (=120 lbs. per square inch). At this pressure, when employing about 3 per cent of lime with the fat, it is practically completely hydrolysed. The autoclaves in use are illustrated by Figs. 11 and 12. That shown in Fig. 11 consists of a cylindrical vessel made of copper, strong enough to withstand a working pressure of eight atmospheres, and provided with an internal steam pipe which reaches the bottom of the vessel. In Fig. 11 the steam leaves at the bottom of the serrated cone, and is thus divided into a number of streamlets which churn the mixture of fat and water into a thorough emulsion. The water and fat, in the proportion of 1 to 3, or 1 to 4, as also the milk of lime, are fed through the funnel-shaped vessel at the side of the autoclave.

The following tables will be found of assistance to the works chemist :—

Milk of Lime in Degrees Baumé obtained from 1 *Kilogram of Caustic Lime*

1 Kilogram Caustic Lime yields Milk of Lime of		Weight of Milk of Lime.	1 Kilogram Caustic Lime yields Milk of Lime of		Weight of Milk of Lime.
Degrees Baumé.	Litres.	Kilograms.	Degrees Baumé.	Litres.	Kilograms.
10	7·50	9·44	38	3·39	5·07
11	7·10	9·01	39	3·37	5·05
12	6·70	8·60	40	3·35	5·03
13	6·30	8·20	41	3·34	5·01
14	5·88	7·80	42	3·32	5·00
15	5·50	7·43	43	3·31	4·98
16	5·25	7·16	44	3·30	4·96
17	5·01	6·92	45	3·29	4·95
18	4·80	6·70	46	3·28	4·93
19	4·68	6·51	47	3·27	4·92
20	4·42	6·38	48	3·26	4·90
21	4·24	6·18	49	3·25	4·89
22	4·16	6·05	50	3·24	4·88
23	4·05	5·92	51	3·23	4·87
24	3·95	5·81	52	3·220	4·86
25	3·87	5·72	53	3·215	4·85
26	3·81	5·63	54	3·210	4·84
27	3·75	5·56	55	3·205	4·83
28	3·70	5·49	56	3·200	4·82
29	3·65	5·43	57	3·195	4·81
30	3·60	5·36	58	3·190	4·800
31	3·56	5·31	59	3·185	4·795
32	3·52	5·27	60	3·180	4·790
33	3·49	5·22	61	3·175	4·780
34	3·47	5·19	62	3·170	4·775
35	3·45	5·16	63	3·165	4·770
36	3·43	5·13	64	3·160	4·760
37	3·41	5·10	65	3·150	4·750

Percentages of Caustic Lime in Milk of Lime

Degrees Baumé.	Per cent.	100 Litres contain Kilograms CaO.	Degrees Baumé.	Per cent.	100 Litres contain Kilograms CaO.
10	10·60	13·3	38	19·72	29·5
11	11·12	14·2	39	19·80	29·6
12	11·65	15·2	40	19·88	29·8
13	12·16	16·1	41	19·95	29·9
14	12·68	17·0	42	20·03	30·1
15	13·20	18·0	43	20·10	30·2
16	13·72	18·9	44	20·16	30·3
17	14·25	19·8	45	20·22	30·4
18	14·77	20·7	46	20·27	30·5
19	15·23	21·6	47	20·32	30·6
20	15·68	22·4	48	20·37	30·7
21	16·10	23·3	49	20·43	30·7
22	16·52	24·0	50	20·48	30·8
23	16·90	24·7	51	20·53	30·9
24	17·23	25·3	52	20·57	31·0
25	17·52	25·8	53	20·62	31·1
26	17·78	26·3	54	20·66	31·1
27	18·04	26·7	55	20·70	31·2
28	18·26	27·0	56	20·74	31·3
29	18·46	27·4	57	20·78	31·3
30	18·67	27·7	58	20·82	31·4
31	18·86	27·9	59	20·85	31·4
32	19·02	28·2	60	20·89	31·5
33	19·17	28·4	61	20·93	31·5
34	19·31	28·7	62	20·97	31·6
35	19·43	28·9	63	21·00	31·6
36	19·53	29·1	64	21·03	31·7
37	19·63	29·3	65	21·05	31·7

Sulphuric Acid required to saturate 100 *Kilograms of Lime*

Degrees Baumé.	Containing Acid of 66° Baumé. Per cent.	Kilograms Acid required for 100 Kilograms CaO.	Kilograms Water to be added to 100 Kilograms Acid to obtain Acid of Degrees Baumé.				
			5° B.	10° B.	15° B.	20° B.	25° B.
66	100·0	175·0	2477	1318	831	554	400
65	97·04	180·3	2471	1313	826	548	395
64	94·10	186·0	2465	1303	820	543	389
63	91·16	196·5	2455	1297	810	532	380
62	88·22	198·4	2451	1294	807	529	376
61	85·28	205·2	2446	1288	801	525	370
60	82·24	212·5	2439	1280	794	516	362
59	80·72	216·8	2434	1276	789	512	358
58	79·12	221·2	2430	1272	785	508	354
57	77·52	226·0	2425	1267	780	503	349
56	75·92	230·5	2421	1263	775	498	344
55	74·32	235·4	2416	1255	770	494	339
54	72·70	240·7	2411	1252	765	488	334
53	71·17	245·9	2405	1247	760	481	328
52	69·30	252·5	2399	1241	754	476	322
51	68·05	257·2	2394	1235	748	471	318
50	66·49	263·3	2386	1230	743	465	314
49	64·37	271·9	2379	1222	734	457	303
48	62·80	278·7	2372	1214	727	450	297
47	61·32	285·4	2366	1208	721	443	289
46	59·85	292·4	2359	1201	714	436	272
45	58·05	302·0	2340	1188	704	427	273

When the autoclave is charged, steam is turned on and the vessel is kept at a pressure of eight atmospheres for about eight to ten hours.

The progress of hydrolysis is controlled by drawing samples from time to time, and ascertaining the amount of free fatty acids, in the manner illustrated by the example given in Vol. I. Chap. XI. It should be noted that the samples contain lime soap, and it is therefore necessary to boil them with dilute sulphuric acid so as to obtain a mixture of neutral fat and free fatty acids.

The following table illustrates the sampling of tallow saponified in an autoclave with 3 per cent of lime, at a pressure of eight atmospheres:—

Sample	taken after the	1st	hour	contained	38·55	per cent	free fatty acids.
,,	,,	2nd	,,	,,	77·40	,,	,,
,,	,,	3rd	,,	,,	83·9	,,	,,
,,	,,	4th	,,	,,	87·5	,,	,,
,,	,,	5th	,,	,,	88·6	,,	,,
,,	,,	6th	,,	,,	89·3	,,	,,
,,	,,	7th	,,	,,	93·0	,,	,,
,,	,,	8th	,,	,,	97·5	,,	,,
,,	,,	9th	,,	,,	98·1	,,	,,
,,	,,	10th	,,	,,	98·6	,,	,,

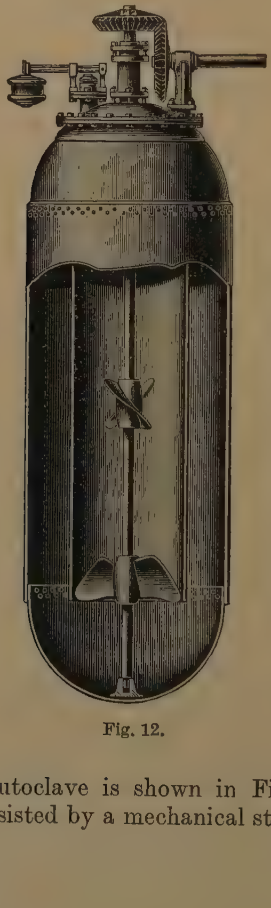

Fig. 12.

Another form of autoclave is shown in Fig. 12; the agitation, effected by steam, is assisted by a mechanical stirring arrangement.

A horizontal form of autoclave fitted with a stirring arrangement of a different kind is illustrated by Fig. 13.

Since the cylindrical autoclaves are liable to be bulged out by the high pressure, they would at last, if the bulging took place progressively in a regular manner, assume the shape of a sphere. Hence spherical autoclaves (first suggested by *L. Bottaro* of Genoa) are also in vogue.

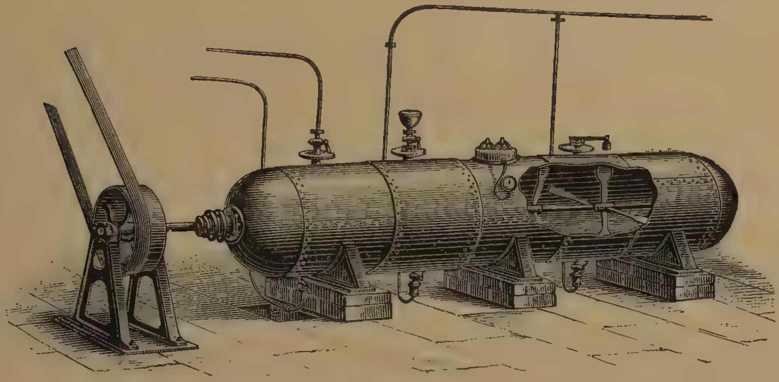

Fig. 13.

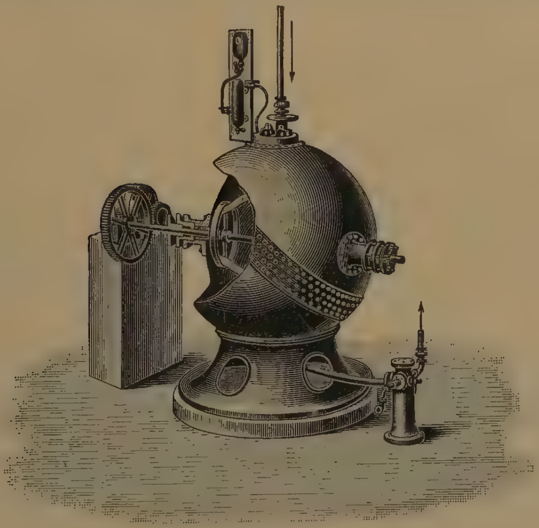

Fig. 14.

An autoclave of this kind, provided with a stirring arrangement, is shown in Fig. 14.

A large number of modifications in the apparatus, purporting to effect a better intermixture of the bases with fat and water, have been proposed during recent years. Since none of them has been able to replace the above-described autoclaves, the specifications of the patentees can only be referred to briefly.[1] *Perrelet* claims [2] to promote intermixture by pulverising the reacting masses by means of steam injectors. In the author's opinion the injectors would become blocked up very soon. *O. Mannig* [3] places a kind of fractionating column on the autoclave.

In the processes considered here the hydrolysis reaches as high a figure as 98-99 per cent. If the temperature, time, and amount of reagent be reduced, the hydrolysis will not reach so high a degree, only about 96-97 per cent of free fatty acids being formed. When the saponification is deemed to be complete, the saponified mass is allowed to stand in the autoclave until it has separated into two layers: glycerin water—"sweet water"—and an upper layer of fatty acids, containing as much lime soap as corresponds to the lime introduced into the autoclave. These two layers are either pumped separately into store vats or, in order to save time, and also to keep the autoclave from standing idle, the whole mass may be pumped into a settling vat, where the separation into two layers takes place. The further working up of the glycerin solution into "crude saponification glycerin" will be considered under the heading "Glycerin," below. The fatty layer is boiled up with steam, and sufficient sulphuric acid [4] is added to decompose the lime soap. On allowing to stand, most of the calcium sulphate separates out at the bottom of the aqueous layer, whereas the fatty acids form a clear oily layer on the top. They are washed carefully with dilute acid to remove the last traces of lime. Some manufacturers precipitate the lime in the last stages as oxalate.

In place of lime, magnesia,[5] and zinc oxide, to which latter also zinc dust is added,[6] are also employed as "accelerators." The advantages which magnesia and zinc oxide offer would lie in that they do not yield a precipitate on decomposing the autoclaved fatty matter with sulphuric acid. This advantage is, however, counterbalanced by the fact that hydrolysis is not so readily effected by means of magnesia, at any rate in the case of tallow and palm oil, as by means of lime. Experience gained on a large scale has shown that tallow, autoclaved with 3 per cent of magnesia under the same conditions as with 3 per cent of lime, is hydrolysed only to the extent of about 96 per cent. In order to reach as good a result as is obtained by means of lime, the working pressure or (and) the length of time must be increased, as will be readily gathered from the theoretical principles explained in Vol. I. Chap. II. This is indeed borne out by the experiments, due to *Kassler*,[7] given in the following table. They should be looked upon as a corollary to the table given above (p. 224).

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[1] Cp. L. Rivière, French patent 352,182; C. Mason, F. G. Geldart, and P. J. Fryer, English patent 7561, 1907.

[2] French patent 322,777; United States patent 736,007; German patent 155,542; English patent 15,586, 1902.

[3] German patent 160,111, and German Registered Trade Mark 219,275.

[4] L. Rivière, French patent 10,495 (3rd edition to French patent 374,179) patents the employment of sodium bisulphate (nitre cake) in place of sulphuric acid.

[5] First proposed by Freestone, English patent 7573, 1884.

[6] Patented by Michaud.

[7] *Seifensieder Zeit.*, 1902, 312.

Saponification of Shea Butter with 3 *per cent of Magnesia at a Pressure of* 9 *Atmospheres*

	Free Fatty Acids. Per cent. *a.*	Free Fatty Acids. Per cent. *b.*
Sample taken after the 1st hour contained . . .	61·4	63·2
„ „ 2nd „ . . .	80·2	81·9
„ „ 3rd „ . . .	90·2	90·1
„ „ 4th „ . . .	91·1	94·8
„ „ 5th „ . . .	95·4	95·7
„ „ 6th „ . . .	95·5	97·1
„ „ 7th „ . . .	96·6	97·1
„ „ 8th „ . . .	98·1	98·0

The pressure being higher than in the case of lime, discoloration of the fatty acids takes place to a somewhat greater extent, and the resulting "sweet water" is more dilute. The chief disadvantage of magnesia lies, however, in the fact that it frequently gives emulsions, which are very troublesome, as they do not separate even after prolonged standing, and also that the saponification is less complete.

Zinc oxide does not offer these disadvantages, but its higher cost outweighs the benefit derived from its use. A small percentage of zinc oxide or zinc dust is, however, frequently used conjointly with lime, as the discoloration of the fatty acids is thereby somewhat diminished (cp. "Soap Manufacture").

Ammonia, which (as a strong base) assists the hydrolysis of fats by water, has frequently been suggested and patented as a saponifying agent.[1] The properties of ammonia render it imperative to carry out the hydrolysis under pressure, and several inventors have patented special autoclaves for this purpose. As none of these suggestions has found practical application, the reader must be referred to the patents mentioned in the footnote.[2] *Barbé, Garelli, and de Paoli* [3] claim that the total ammonia used is recovered by treating the ammonia soaps formed in a current of steam, when ammonia is volatilised whilst the free fatty acids remain behind.

As a curiosity, there may also be mentioned the proposal [4] to use aluminium soaps (of fatty acids or of rosin acids).

According to the fatty material employed, the composition of the resulting fatty acids will naturally vary. The chief materials employed hitherto, at any rate in this country, in the saponification processes described above, are tallow and palm oil,[5] or a mixture of both ; hence it may be taken that the fatty acids consist approximately of 50 per cent of solid acids and 50 per cent of oleic acid. Bone fat, especially on the Continent, is also largely "autoclaved" for candle-making purposes. The kind employed for this purpose is benzine-extracted bone fat, which is unsuitable for soap-making purposes. Since candles made exclusively from bone fat stearine are soft and friable, it is customary to make up the charges for the autoclave from a mixture of bone fat and other fats. With regard to goat's tallow as a candle material see Vol. II. "Tallow." Under bone fat are also comprised "Greases" (see Chap. XVI.).

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[1] Cp. Vol. I. Chap. I.

[2] Barbé, Garelli, and de Paoli protect the use of ammonia by French patent 372,341 and 1st Addition No. 9255 ; cp. also Glatz, United States patent 819,646.

[3] German patent 209,537.

[4] Ruch, French patent 371,416.

[5] Palm oil was first suggested as a candle-making material by Hempel and Blundel in 1836.

"Cotton seed stearine" of a high titer test—above 40° C.—is also used to some extent as a raw material for candle-making purposes.

In the United States that lard stearine which is unfit for edible purposes is not infrequently converted into candle material by the autoclave process. A sample of such material examined in the author's laboratory had the melting point 125° F. = 51·7° C.

The employment of palm oil is somewhat restricted on the Continent, and other vegetable fats—such as vegetable tallow, shea butter, mowrah seed oil—are in use. The commercial exploitation of the large supplies of vegetable fats suitable for the candle industry has not yet, however, attracted such attention from importers as this subject deserves.[1] Recently ucuhuba fat has been "patented" as a candle-making material (see Vol. II.).[2]

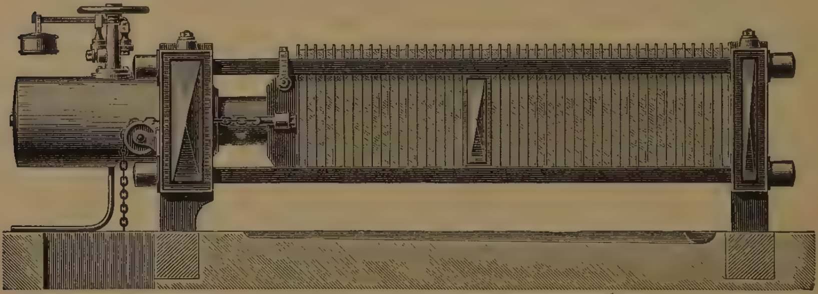

Fig. 15.

Since oleic acid is useless as a candle material, the next operation is to effect its removal from the mixed fatty acids. Hitherto this has been principally effected by pressing the mixed fatty acids. The crude acids, after being thoroughly freed from mineral acid, are run into shallow trays arranged in tiers, in which the fatty acids are allowed to crystallise. These trays of nickel-plated metal are best placed in a room which can be kept at any desired low temperature; hence this room is fitted with cooling coils fed with cold brine from a refrigerating plant. The temperature at which the crystallisation takes place is carefully regulated, so as to obtain well-formed crystals of stearic and palmitic acids embedded in the mother liquor of oleic acid. If the fatty acids are cooled too rapidly, they solidify to an amorphous mass, from which it is extremely difficult to express the oleic acid satisfactorily (the mass " spues "). The solidified mass is taken out of the trays and pressed, at first at the ordinary temperature in a cold press, such as is shown in Fig. 15. The bulk of the oleic acid—" red oil "—is thereby removed. The hard cakes still contain too much oleic acid, and are therefore pressed a second time, at a somewhat higher temperature, in a hot press (Fig. 16), the cakes being placed in a bag of horse-hair, or other suitable material, between two press plates which are heated by live steam. In the figure shown the steam is supplied from above; but since the stuffing-boxes, owing to the wear and tear to which they are subjected, require frequent renewing, the steam is supplied in more modern presses from below.

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[1] Cp. Lewkowitsch, Cantor Lectures, *Journ. Soc. Arts*, 1904.

[2] Companhia Luz Stearica, French patent 394,362.

The cakes are allowed to stand under pressure in the hot until a sufficient amount of oleic acid has been expressed to leave them white, ready to be melted (after a further purification to remove the last traces of lime) and to be moulded into candles. The oleic acid which runs from the hot-pressed cakes contains a considerable amount of solid acids (" stearine "). They are recovered either by admixing the material to a fresh batch of the original fatty acids, or by subjecting it, together with the " red oil," to a process of cooling in the refrigerating plant.

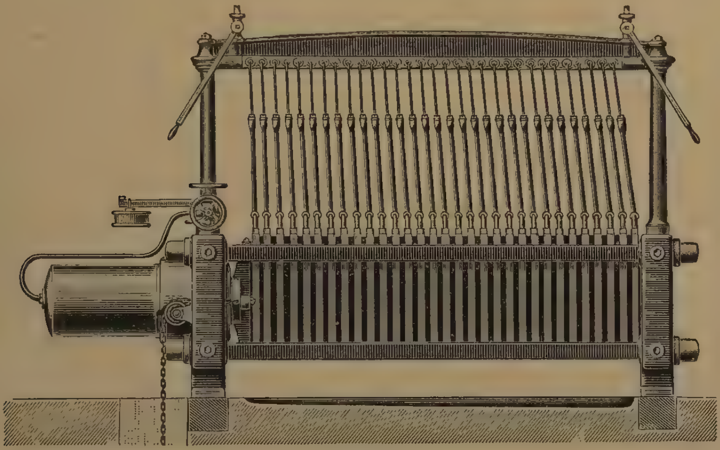
Fig. 16.

If the " stearine " be not sufficiently white, the mixed fatty acids are subjected to distillation previous to being pressed (see p. 239).

Another method, patented by *Lanza*,[1] for separating oleic acid from the solid acids dispenses altogether with the cold and hot presses. This method is based on the property of a dilute solution of stearosulphuric acid (prepared by dissolving the product of reaction of concentrated sulphuric acid on oleic acid in water) to dissolve oleic acid only, whereas the solid fatty acids remain undissolved.[1] The solid fatty acids are separated from the liquid acids by filtration much in the same manner as crystals are separated from their mother liquor. The author has seen this process carried out on a large scale ; the solid acids so obtained were as good in colour as those obtained in the hot press.

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[1] French patent 352,337; French patent 366,457; English patent 11,877, 1906; German patent 191,238.

The proposal patented by *Chevreul and Gay-Lussac* in 1825, viz. to separate the solid acids from the oleic acid by alcohol, has been again subjected to an experimental examination by *Pastrovich*,[2] but neither his efforts nor those of *Charitschkoff*[3] to effect the same purpose by means of benzene and alcohol have any practical interest.

For the separation of solid from liquid acids by means of their ammonium soaps in a current of steam, when the ammonium soaps of the solid acids are decomposed first, or by dissolving the mixed ammonium soaps in cold water, in which the oleate is easily soluble, whereas the palmitic and stearic oleates are sparingly soluble, cp. *Barbé, Garelli, and de Paoli.*[4] A method involving the use of a centrifugal machine has been patented by *C. H. Hapgood.*[5]

The amount of oleic acid in the cold-pressed (or hot-pressed) cakes is most rapidly determined by ascertaining the iodine value of the material. In this manner the pressing operations are readily controlled. (It should be noted that the expressed " oleine " contains most of the neutral fat which has escaped saponification in the autoclave process.) For the rapid conversion of the iodine values into percentages of oleic acid, the following table, calculated by *Mangold*, may be found useful in a works laboratory. The " stearine " of the table represents a mixture of palmitic and stearic acids.

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[1] Cp. Vol. I. Chap. VIII. Essentially the same process is patented by Twitchell, United States patent 918,612, using the sulpho-fatty aromatic acid.

[2] *Chem. Revue*, 1904, 1.

[3] *Ibid.*, 1905, 106.

[4] German patent 209,537.

[5] U.S. patent 1,381,705, 1921.

[TABLE

Iodine Value.	Product contains		Iodine Value.	Product contains		Iodine Value.	Product contains	
	Oleic acid. Per cent.	"Stearine." Per cent.		Oleic acid. Per cent.	"Stearine." Per cent.		Oleic acid. Per cent.	"Stearine." Per cent.
0	0	100	31	34·41	65·59	62	68·83	31·17
1	1·11	98·89	32	35·52	64·48	63	69·94	30·06
2	2·22	97·78	33	36·63	63·37	64	71·05	28·95
3	3·33	96·67	34	37·74	62·26	65	72·16	27·84
4	4·44	95·56	35	38·85	61·15	66	73·27	26·73
5	5·55	94·45	36	39·96	60·04	67	74·38	25·62
6	6·66	93·34	37	41·07	58·93	68	75·49	24·51
7	7·77	92·23	38	42·18	57·82	69	76·60	23·40
8	8·88	91·12	39	43·29	56·71	70	77·71	22·29
9	9·99	90·01	40	44·40	55·60	71	78·82	21·18
10	11·10	88·90	41	45·51	54·49	72	79·93	20·07
11	12·21	87·79	42	46·62	53·38	73	81·04	18·96
12	13·32	86·68	43	47·73	52·27	74	82·15	17·85
13	14·43	85·57	44	48·84	51·16	75	83·26	16·74
14	15·54	84·46	45	49·95	50·05	76	84·37	15·63
15	16·65	83·35	46	51·06	48·94	77	85·48	14·52
16	17·76	82·24	47	52·17	47·83	78	86·59	13·41
17	18·87	81·13	48	53·28	46·72	79	87·70	12·30
18	19·98	80·02	49	54·39	45·61	80	88·82	11·18
19	21·09	78·91	50	55·50	44·49	81	89·93	10·07
20	22·20	77·80	51	56·62	43·38	82	91·04	8·96
21	23·31	76·69	52	57·73	42·27	83	92·15	7·85
22	24·42	75·58	53	58·84	41·16	84	93·26	6·74
23	25·53	74·47	54	59·95	40·05	85	94·37	5·63
24	26·64	73·36	55	61·06	38·94	86	95·48	4·52
25	27·75	72·25	56	62·17	37·83	87	96·59	3·41
26	28·86	71·14	57	63·28	36·72	88	97·70	2·30
27	29·97	70·03	58	64·39	35·61	89	98·81	1·19
28	31·08	68·92	59	65·50	34·50	90·07	100	0
29	32·19	67·81	60	66·61	33·39			
30	33·30	66·70	61	67·72	32·28			

A more direct method of carrying out the valuation of the solid acids is to determine their solidifying point.

The following tables due to *Carlinfanti and Levi-Malvano* may be found useful here :—

Per cent.		Solidifying Point. °C.
Stearic Acid.	Palmitic Acid.	
100	0	68·2
90	10	65·90
80	20	63·50
70	30	60·80
60	40	57·65
50	50	56·25
40	60	55·90
30	70	54·75
20	80	55·75
10	90	58·40
0	100	61

Per cent.		Solidifying Point. ° C.
Stearic Acid.	Oleic Acid.	
0	100	9
5	95	23·45
15	85	34·25
25	75	46·6
35	65	51·90
46	54	55·95
55	45	58·65
65	35	61·25
75	25	63·40
85	15	65·40
95	5	67 15
100	0	68·2

Per cent.		Solidifying Point. ° C.
Palmitic Acid.	Oleic Acid.	
100	0	61
90	10	59·20
80	20	57·30
70	30	55·10
60	40	52·60
50	50	49·75
40	60	46·25
30	70	41·60
20	80	35
10	90	24·80
0	100	9

Y. de Schepper and Geitel[1] recommend each candle-works chemist to construct an empirical table for his own use, from which the yield of candle material can be found at a glance. Such an empirical table is computed by mixing the finished product "stearine" and the finished oleic acid as manufactured in the works in known proportions, and determining the solidifying points of these mixtures. Of course a separate table must be constructed for each kind of fat or mixture of fats, and it must be emphasised that a table of this kind holds good only for the particular works for which it is constructed, as the solidifying points of the mixed fatty acids and the yields of candle material naturally differ considerably under varying conditions :—

The following table, due to *de Schepper and Geitel,* affords the necessary guidance (cp. also table, p. 241) :—

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[1] *Dingl. Polyt. Journ.*, 245, 295.

Solidifying Point of the Mixture.	Stearine of Solidifying Point 48° C.	Solidifying Point of the Mixture.	Stearine of Solidifying Point 48° C.	Solidifying Point of the Mixture.	Stearine of Solidifying Point 48° C.
°C.	Per cent.	°C.	Per cent.	°C.	Per cent.
5·4	...	20	12·1	35	39·5
6	0·3	21	13·2	36	43·0
7	0·8	22	14·5	37	46·9
8	1·2	23	15·7	38	50·5
9	1·7	24	17·0	39	54·5
10	2·5	25	18·5	40	58·9
11	3·2	26	20·0	41	63·6
12	3·8	27	21·7	42	68·5
13	4·7	28	23·3	43	73·5
14	5·6	29	25·2	44	78·9
15	6·6	30	27·2	45	83·5
16	7·7	31	29·2	46	89·0
17	8·8	32	31·5	47	94·1
18	9·8	33	33·8	48	100·0
19	11·1	34	36·6		

If the amount of stearic acid in the material be required, its proportion is ascertained by the method described (Vol. I. Chap. VIII.).

The "stearine" contained in the "red oil" (and in the runnings from the hot press) is recovered in the refrigerating plant by cooling the liquid mass. Various appliances are in vogue. The simplest plan is to refrigerate the oil in large tanks fitted with a row of coils through which cooled brine or calcium chloride solution is pumped. Some manufacturers cool small quantities in mixing vessels, so as to be able to stir the cooled mass. The process requires attention, as the success of the operation depends on the separation of well-formed crystals. These are readily separated from the oleic acid by means of a filter-press.

A more rapid method of cooling consists in allowing the red oil to run over a refrigerating wheel—*Petit's* wheel, Fig. 17 (cp. "Lard Cooling," Vol. II. Chap. XIV.). This wheel is shown partly in section. The cooled brine enters at C, runs along the circumference of the wheel, and leaves at the opposite side. The oleine is fed into trough *f*, into which dips the rotating wheel, carrying with it upwards a thin film of oleic acid, which is thus rapidly cooled, and deposits crystals of "stearine." The crystalline mass on reaching the scraper *h* is scraped off and the sludgy mass is collected in the cooled vessel F, from which it is pumped through pump P into a filter-press. The crystals form an intermediate product, and are mixed with the crude candle material at a suitable stage of the process.

In place of *Petit's* wheel the cooler used in the lard industry (Vol. II. p. 702) may be employed. The greatest attention must be paid to the production of well-formed crystals, which is most readily obtained by slow cooling.

Yield of the Process.—The yield of candle material by the autoclave process depends, of course, on the melting points of the finished "stearine," and on the completeness with which the "stearine" is recovered from the " red oil." It may, however, be taken as sufficiently accurate that the amount of high melting " stearine " from tallow or palm oil, or a mixture of both, varies from 45 to 47 per cent of the raw material, about 30 per cent being obtained from the hot press and the remainder from the refrigerated " red oil." The proportion of finished oleic acid, " oleine," amounts to 47-48 per cent. If a stearin of somewhat lower melting point be aimed at, the yield of stearine may reach 50-52 per cent, with a consequent lower yield of oleic acid. In the case of good tallow, the yield of " saponification crude glycerin " of specific gravity 1·240 reaches 10 per cent. This is summarised in the following table :—

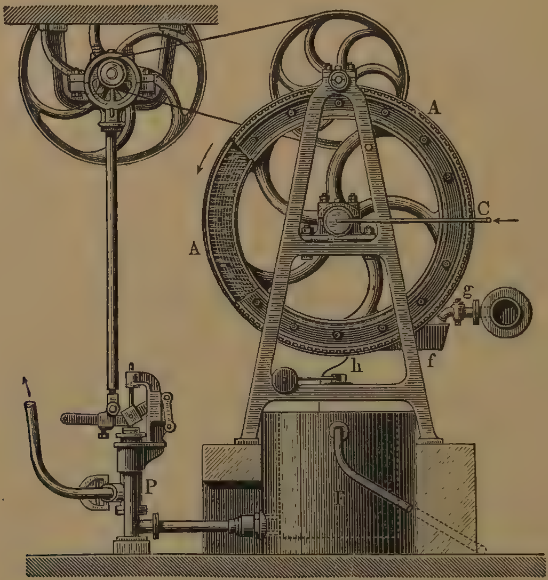

Fig. 17.

Yield from 100 *parts of Tallow by the Autoclave Process*

	High Melting Stearin.	Lower Melting Stearin.
Candle material (stearic and palmitic acids)	45-47 parts	50·52 parts
Oleic acid (containing unsaponified fat)	48-47 "	43-42 "
Crude glycerin, specific gravity 1·240	10-10 "	10-10 "
	103-104 parts	103-104 parts

The " stearine " is used as candle material either as such, or in admixture with paraffin wax, etc. (see below). The oleic acid, " oleine," is either converted into textile soap or used as a wool oil (cp. p. 103). In the mixed process (see below) part of the oleic acid is converted into candle material.

The production of "crude saponification glycerin" from the "sweet water" will be described under "Glycerin."

If the fatty acids obtained by the autoclave process be too dark, and hence do not yield a sufficiently white candle material, they must be purified by distillation.[1] This is carried out in the same apparatus which is described under "Sulphuric Acid Saponification," and in the same manner as is detailed under "Mixed Process" (see below).

Preparatory to the distillation the fatty acids are washed with dilute sulphuric acid to remove mineral substances (soaps, etc.) and finally washed free from acid and dried (see p. 238).

In the distilling process the fatty acids do not undergo a chemical change (cp. Vol. I. Chap. III.), provided due care be observed in conducting the distillation. Since, however, the autoclaved mass contains some small proportion of unsaponified fat, which goes on accumulating in the still—especially if the still be fed continuously—decomposition of the unsaponified fat finally takes place with formation of hydrocarbons ("Destructive Distillation," see Vol. I. Chap. I.). (In the case of autoclaved *extracted* bone fat, small amounts of hydrocarbons appear at the outset of the distillation.) *Kassler* [2] has shown that, if during the progress of distillation so much neutral fat has accumulated that its proportion reaches 12 to 15 per cent of the still contents, hydrocarbons are formed.[3] Hence those portions of the distillate which are caught towards the end of the "run" are collected separately ("Still Returns") and redistilled.

In the following table the author has compiled in tabular form the results of a number of large-scale experiments made by *Kassler* [4] with fatty acids from several kinds of fats. The neutral fats were hydrolysed in an autoclave with 2·6 to 3 per cent of magnesia at a pressure of 9 atmospheres; the autoclaved mass was freed from magnesia by dilute sulphuric acid :—

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[1] Dreymann, German patent 21,838.

[2] *Chem. Revue,* 1903, 151.

[3] Winter (German patent 170,563) states that the formation of hydrocarbons does not take place in the case of coconut and palm nut oils. When these two oils were hydrolysed to an extent of 90 per cent the fatty acids are said to be completely removable by distillation *in vacuo* without any of the neutral fat becoming decomposed.

[4] *Chem. Revue,* 1902, 49; *Seifensieder Zeit.,* 1902, 311, 329.

Yield from Autoclaved Fatty Acids on Distillation

No.	From	Quantity distilled.	Duration of Distillation.	Distillate for Presses.	"Still-Returns."	"Stearine Pitch."
		Tons. About	Hours.	Per cent.	Per cent.	Per cent.
1	Tallow stearine	8	36	95·6	2·1	2·3
2	Vegetable tallow	5	35	92·4	4·0	3·6
3	Tallow	5	36	94·2	2·3	3·5
4	Bone fat	5	38	91·5	5·0	3·5
5	Palm oil	5	37	91·3	4·5	4·2
6	Shea butter	5·3	29	94·1	2·4	3·7

In the following table, due to *Kassler*,[1] are recorded the solidifying points and the proportions of oleic acid calculated from the iodine values of the distillates, as obtained from hour to hour, during a "run":—

Distillation of Autoclaved Fatty Acids

Samples taken after Hours.	Tallow Acids of Solidifying Point 41·7° C., containing: Oleic Acid, 41·5 per cent; Neutral Fat, 3·6 per cent.			Bone Fat Acids of Solidifying Point 39·8° C., containing: Oleic Acid, 60·4 per cent; Neutral Fat, 2·5 per cent.			Palm Oil Acids of Solidifying Point 41·6° C., containing: Oleic Acid, 60·4 per cent; Neutral Fat, 2·9 per cent.			Shea Butter Acids of Solidifying Point 48·4° C., containing: Neutral Fat, 2 per cent.		
	Solidifying Point.	Oleic Acid.	Hydrocarbons.	Solidifying Point.	Oleic Acid.	Hydrocarbons.	Solidifying Point.	Oleic Acid.	Hydrocarbons.	Solidifying Point.	Iodine Value.	Hydrocarbons.
	°C.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	°C.	Per cent.	Per cent.
5	40·4	38·0	...	37·2	54·9	...	43·8	56·0	...	48·9	47·24	...
6	40·4	38·3	...	38·1	54·9	...	43·8	56·2	...	49·7	47·72	...
7	40·7	38·9	...	38·1	55·7	...	43·8	56·3	...	50·5	48·05	...
8	40·9	38·9	...	38·3	56·2	...	43·5	56·7	...	50·4	48·04	...
9	41·2	39·5	...	38·7	56·5	...	43·4	56·9	...	49·8	48·37	...
10	41·3	39·9	...	38·8	57·0	...	43·1	57·6	...	50·3	48·50	...
11	41·3	40·5	...	38·9	57·6	...	42·4	58·8	...	50·3	48·50	...
12	41·3	41·0	...	38·9	58·1	...	42·2	59·0	...	50·8	48·71	...
13	42·5	41·2	...	39·2	58·5	...	42·0	59·0	...	50·8	48·77	...
14	42·7	41·5	...	39·2	59·4	...	41·0	59·0	...	50·9	48·97	...
15	42·9	41·7	...	39·2	59·8	...	40·8	59·5	...	51·3	49·14	...
16	43·0	42·0	...	39·4	59·9	0·5	40·5	59·5	...	51·3	49·29	...
17	43·2	42·5	...	39·5	60·7	0·9	40·1	59·7	0·5	51·0	50·56	...
18	43·4	42·5	...	39·8	60·9	1·3	39·8	59·9	1·1	50·7	51·00	...
19	43·6	42·5	...	40·0	61·2	1·8	39·8	60·4	1·7	51·1	51·62	...
20	44·5	42·7	...	40·5	61·2	2·2	39·3	60·8	2·3	51·1	51·73	...
21	44·5	42·7	0·2	40·3	61·4	2·9	39·2	61·1	2·8	50·9	51·40	...
22	44·6	42·8	0·8	40·3	61·6	3·5	39·1	62·0	4·0	50·9	51·18	...
23	43·2	43·0	1·2	40·0	61·8	3·8	38·2	62·7	4·5	51·2	51·23	...
24	42·5	43·1	1·7	39·0	62·0	4·2	38·0	63·4	5·1	51·3	51·32	...
25	40·0	43·0	2·9	39·0	62·1	4·5	38·0	63·8	5·1	51·3	51·42	0·34
26	...	...	...	...	...	...	...	...	...	51·4	51·59	0·78
27	...	...	...	...	...	...	...	...	...	51·5	51·68	0·92
28	...	...	...	...	...	...	...	...	...	51·3	51·79	2·80
29	...	...	...	...	...	...	...	...	...	51·3	51·64	3·56
30	...	...	...	...	...	...	...	...	...	50·8	51·52	5·07

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[1] *Seifensieder Zeit.*, 1902, 349.

(3) Sulphuric Acid Saponification, Hydrolysis by means of Concentrated Sulphuric Acid

The theory of this process of hydrolysis has been discussed in Vol. I. Chap. II. The technical operation [1] consists in rapidly intermixing fat which has been heated previously to a temperature of 120° C. or more (and thereby freed from the last traces of moisture) with 4 to 6 per cent of concentrated sulphuric acid of 66°-67° Baumé. If sulphuric acid of lower strength be used, the hydrolysis is not complete, as will be gathered from the table given in Vol. I. Chap. II. With the decrease of the strength of sulphuric acid, hydrolysis decreases rapidly; an acid of 60 per cent SO_4H_2 is no longer capable of effecting hydrolysis on a practical scale. The behaviour of sulphuric acid to the saturated glycerides is of little practical importance, since sulphonated compounds (of the glycerides as well as of the saturated fatty acids) that are formed (if any) are subsequently decomposed, yielding the original saturated acids practically unchanged. With olein, however (the less saturated glycerides need not be considered here, being of no practical importance in the manufacture of "Stearine"), the sulphuric acid forms saturated sulphonated compounds, a small quantity of sulphurous acid being at the same time evolved in consequence of secondary reactions setting in. These sulphonated compounds have the property of being somewhat readily hydrolysed on boiling with water (cp. tables, Vol. I. Chap. II.).

The higher the temperature to which the fat has been heated, and the larger the percentage of sulphuric acid used, the more copious is the evolution of sulphurous acid and the further will the secondary reactions proceed. In order to reduce the destruction (carbonising) of organic matter, which necessarily leads to a lower yield of fatty acids, and especially of glycerin, great attention must be paid to the following factors; the preliminary purification of the fatty matter (by boiling with dilute sulphuric acid, etc.), the complete removal of moisture by heating over dry steam coils, quantity of sulphuric acid, temperature, and time during which the acid is allowed to act on the fat. In order to ensure the most intimate contact of the fat with the acid within the shortest possible time, various mixing machines are used. Mixing by means of air cannot be recommended, as this leads to deterioration of the material and to appreciable losses. One type of apparatus is shown in Fig. 18. Other devices consist in pulverising the fatty matter by centrifugal force, etc.

The sulphonated mass is next run into boiling water and agitated by steam until the sulphonated compounds are hydrolysed. On allowing to stand, separation into two layers takes place: a lower aqueous layer containing the sulphuric acid employed and also the glycerol, and an upper layer of fatty material.

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[1] Cp. W. C. Jones and G. F. Wilson, English patent 9542, 1842; G. Gwynne and G. F. Wilson, English patent 10,000, 1843; G. F. Wilson, G. Gwynne, and J. P. Wilson, English patent 10,371, 1844; Fremy's French patent dates from the year 1855; Dubovitz, English patent 2989, 1910.

This fatty material, is, as a rule, so dark that it cannot be worked up by pressing immediately after solidifying, in the manner described under (2). In order to obtain material of good colour the fatty mass must be distilled. A type of apparatus employed for this purpose is illustrated by Fig. 19. The fatty material, thoroughly freed from mineral acid by washing with water, is charged into still A, where it is heated at first by direct fire. When the material is sufficiently hot, a current of steam, dried preliminarily in P and superheated in S, is introduced through P_1, and the fatty acids are thus carried over through D into the cooling worm R. The acids and the condensed water run into box X, where their separation takes place, and any vapours escape through G. The fatty material which is drawn off at Z represents a mixture of liquid acids and candle material, which is pressed in the cold and subsequently in the hot as described above (p. 229). A large number of patents have been taken for special forms of stills and for processes claiming continuous feeding, distillation *in vacuo*, or both combined. The ovoid shape of the still shown in Fig. 19 has been largely replaced by stills of lenticular shape. In order to reduce the height to which the vaporised fatty acids must rise, as thereby the pressure must be increased, the condensing arrangements also vary widely. In the plant shown in Fig. 19 the whole distillate is obtained in one mass. Some manufacturers collect the distillate in several fractions, whereby the subsequent separation into solid and liquid material is somewhat simplified. This is attained by combining air cooling of the hottest distillate with water cooling of the less hot distillates. The portions distilling over towards the end of the "run" are so dark coloured and contaminated with organic impurities (which as a rule is the case when the amount of neutral fat has accumulated in the still, so as to form about 12 per cent of its contents) that they must be redistilled, hence they are termed "still returns" (German, *Blasenretourgang*). The distillation of such "still returns" is exemplified by the second table, p. 242. The best practice is to stop the distillation when dark-coloured distillates make their appearance and to remove

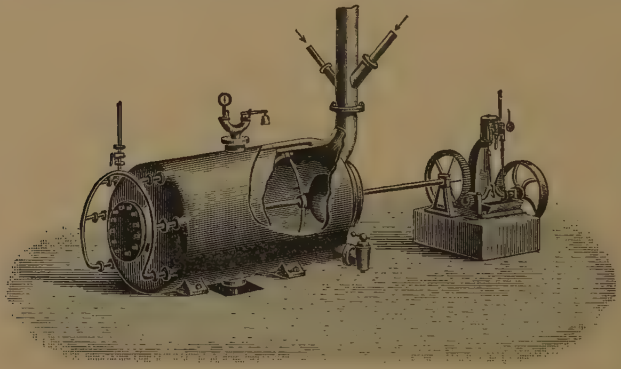

Fig. 18.

the still residue into a second still, where the residues from several "runs" are allowed to accumulate. These are then distilled separately, preferably *in vacuo*, and the distillation is carried so far that only pitch remains in the still (see "Stearine Pitch," p. 260). In some works the residues are again treated with concentrated sulphuric acid to hydrolyse the neutral fat accumulated therein and to remove the accumulated mineral matter (chiefly iron or copper derived from the material of the still). After washing out the acid, etc., the mass is subjected to the second distillation, until "hard pitch" is obtained (see p. 260). The fatty acids obtained are dark (especially the first and last runnings); hence they are redistilled by being admixed in small proportions with crude fatty acids undergoing their first distillation. In order to obtain a good yield it is essential that the fat has been hydrolysed as completely as possible or, in other words, that the crude fatty acids to be distilled contain a very small amount of neutral fat. A high proportion of neutral fat gives rise to hydrocarbons which impair the crystallisation of the stearine.

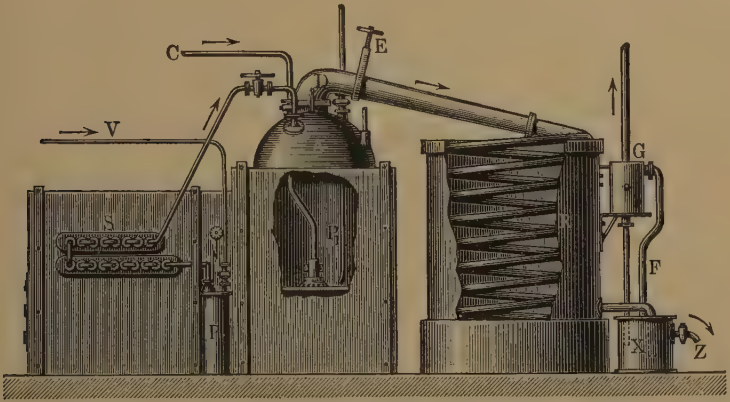

Fig. 19.

The acid saponification process leads to a greater yield of solid material than does the autoclave process. Whereas the candle material obtained by the latter process may reach 52 per cent (see p. 234), the yield of "stearine" by sulphuric acid saponification is from 61 to 63 per cent; hence only 30-32 per cent of oleic acid results as a by-product in this process, as against 47 per cent from the autoclave process.

It is therefore evident that a certain amount of oleic acid has been converted into solid material. The chemical change taking place has already been incidentally explained in Vol. I. Chap. III. Owing to the great technical importance of this chemical change, the "conversion of oleic acid into candle material" will be fully considered below (p. 244). It may therefore suffice here to state that in the acid saponification process from 15 to 17 per cent of oleic acid is converted into solid products, chiefly into stearolactone and isomeric solid oleic acid

(" iso-oleic " acid, see Vol. I. p. 194), with which small quantities of ι-hydroxystearic acid may be admixed.

In the early years of candle manufacture the acid saponification process was applied to tallow and other fats of good quality on account of the higher yield of candle material, the great loss of glycerin being then considered of minor importance. Since, however, the remunerative recovery of glycerin has led to the adoption of the " mixed process " for the treatment of fat of good quality, it has become—almost generally—the practice to treat by this process low-class material, such as " greases" and all kinds of " waste fats " (Chap. XVI.). This process commends itself all the more in these cases, as on " autoclaving " such low-class fats extremely persistent emulsions are formed which frequently retain the glycerin so firmly entangled that it can only be separated with the greatest difficulty. Moreover, the increased amount of solid material leads to a better crystallisation of the resulting fatty acids.

The progress of hydrolysis of the acidified fat is best controlled in the manner illustrated by the table given in Vol. I. Chap. II.

The examination of the press cakes (from the cold press as well as from the hot press) by means of the iodine absorption test obviously does not lead to the same information as is obtained in the case of autoclaved material, since iso-oleic acid also absorbs iodine. The press operations are therefore best controlled by the determination of the *solidifying point* of the fatty acids with the help of an empirical table worked out for each kind of fat or mixture of fats.

As an example, I give the table on following page, due to *Y. de Schepper and Geitel*,[1] computed in the candle-works of Gouda (Holland) for tallow and palm oil. The first column contains the solidifying points of the various intermediate products up to the finished " stearine." The yields of " stearine " of the solidifying points recorded in the first horizontal column were obtained by pressing the hydrolysed mass at different temperatures.

The stearine obtained by this process is known in commerce under the name " distilled stearine." This " stearine " has a lower solidifying point than " saponified stearine " has. Whereas the titer test of the latter is, as a rule, 132° F. to 134° F., the best commercial " distillation stearine " solidifies at 129° F., or very little above.

The " distilled stearine " consists, therefore, of stearic, palmitic, and iso-oleic acids, with which small amounts of hydroxystearic acid and of stearolactone may be admixed. The amount of stearolactone may be inferred from the difference between the saponification and neutralisation values of the sample (cp. Vol. I. Chap. VIII.).

The proportion of iso-oleic acid can be calculated from the iodine value of the sample, the assumption being made that oleic acid is entirely absent.

Stearic acid is determined direct (Vol. I. Chap. VIII.). The presence of hydroxystearic acid is ascertained by determining the acetyl value (Vol. I. Chap. VI.). The amount of palmitic acid is then found by difference.

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[1] *Dingl. Polyt. Journ.* 245, 295.

The oleic acid resulting as a by-product in this process is termed "distilled oleine," "distillation oleine" (cp. p. 103).

The *crude glycerin* obtained is known as "distillation glycerin" (see below); this term must not, however, be confounded with "distilled glycerin." The amount of recovered crude glycerin for one and the same kind of fat is lower than in the autoclave processes. A definite figure cannot be given, as the yield depends on the care exercised in the first stages of the process. It may, however, be added that in well-managed works the yield from good fats containing a small quantity of free fatty acid amounts to from 8 to 9 per cent of 28° Bé. "distillation glycerin."

Solidifying Point.	Percentage of "Stearine" of Solidifying Point stated.							
	Palm Oil.				Tallow.			
°C.	48°	50°	52°	55·4°	48°	50°	52°	54·8°
5	...	...	...	...	...	...	...	...
10	4·2	3·6	3·3	2·6	3·2	2·7	2·3	2·1
15	10·2	9·8	7·8	6·6	7·5	6·6	5·7	4·8
20	17·4	15·0	14·4	11·0	13·0	11·4	9·7	8·2
25	26·2	22·4	19·3	16·2	19·2	17·0	14·8	12·6
30	34·0	30·5	26·6	22·3	27·9	23·2	21·4	18·3
35	45·6	40·8	35·8	29·8	39·5	34·5	30·2	25·8
36	48·5	43·2	38·0	31·8	42·5	36·9	32·5	27·6
37	51·8	45·5	40·3	33·6	46·0	40·0	34·9	29·6
38	55·5	48·8	42·6	35·8	49·5	42·6	37·5	32·0
39	59·2	51·8	45·6	38·2	53·2	45·8	40·3	34·3
40	63·0	55·2	48·6	40·6	57·8	49·6	43·5	37·0
41	66·6	58·7	52·0	43·0	62·2	53·5	47·0	40·0
42	70·5	62·2	55·2	45·5	66·6	57·6	50·5	42·9
43	74·8	66·0	58·8	48·5	71·8	62·0	54·0	46·0
44	79·2	70·2	62·0	51·4	77·0	66·2	58·4	49·8
45	84·0	74·5	66·0	54·3	81·8	71·0	62·6	53·0
46	89·4	78·8	69·8	57·8	87·5	75·8	67·0	56·8
47	94·3	83·0	74·0	61·0	93·3	80·9	71·5	60·8
48	100·0	88·0	78·6	65·0	100·0	87·2	76·6	65·0
49	...	94·2	83·5	69·1	...	93·0	84·7	69·5
50	...	100·0	89·0	73·4	...	100·0	87·0	74·5
51	...	...	94·5	78·0	...	...	93·5	79·8
52	...	...	100·0	82·8	...	...	100·0	84·8
53	...	...	...	87·6	...	...	...	90·1
54	...	...	...	92·2	...	...	...	95·3
55	...	...	...	97·5	...	...	(54·8)	100·0
55·4	...	...	...	100·0	...	...	...	...

The approximate practical yield from tallow is summarised in the following table :—

[Table

Yield from 100 parts of Tallow by the Sulphuric Acid Saponification Process

Candle material (stearic, palmitic, iso-oleic, hydroxystearic acids, and stearolactone) . . .	61-63 per cent
Oleic acid (containing iso-oleic acid) . . .	30-32 ,,
Crude glycerin, specific gravity 1·240 . . .	8- 9 ,,
Pitch ; Loss	2- 3 ,,
	101-107 ,,

(4) The Mixed Process

From the above-given data regarding the yields of candle material and crude glycerin it will be gathered that, on the one hand, more candle material is obtained in the "acid saponification process" than by autoclaving the fatty materials, whereas, on the other hand, a larger amount of glycerin of better quality results from the autoclave process. Hence a combination of these two processes suggests itself, for as regards increase of candle material the action of sulphuric acid on olein is apparently the same as on oleic acid. The combined method, known as the "mixed process," consists in hydrolysing the fatty material in an autoclave by means of bases, thus recovering the full amount of glycerin, and then treating the fatty material with concentrated sulphuric acid in the manner described under (3) (p. 237). Any neutral fat which has escaped hydrolysis in the autoclave is thus saponified. Therefore, in the subsequent distillation of the acidified material less neutral fat can accumulate in the still than is the case when autoclaved, non-acidified, fatty acids are distilled. Hence the amounts of hydrocarbons in the distillates are also reduced. This will be gathered from a comparison of the following tables, due to *Kassler*,[1] with the corresponding table given on p. 236.

Yield from Autoclaved and Acidified Fatty Acids on Distillation

No.	From	Quantity distilled.		Duration of Distillation.		Distillate for Presses.		"Still-Returns."		"Stearine Pitch."	
		Tons.		Hours.		Per cent.		Per cent.		Per cent.	
		I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
1	Tallow . .	5	7	34	33	94·8	94·6	2·0	2·6	3·2	2·8
2	Bone fat .	5	5·6	35	34	92·8	90·3	4·2	5·4	3·0	4·3
3	Palm oil .	5	5	36	32	91·6	91·0	4·6	5·3	3·8	3·7

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[1] *Seifensieder Zeit.*, 1902, 349 ; *Chem. Revue*, 1902, 50.

Distillation of Autoclaved and Acidified Fatty Acids

Samples taken after Hours.	Tallow Acids of Solidifying Point 42·2° C., containing: Oleic Acid, 29·8 per cent; Neutral Fat, 0·4 per cent.				Bone Fat Acids of Solidifying Point 40·4° C., containing: Oleic Acid, 42·2 per cent.; Neutral Fat, 0·5 per cent.				Palm Oil Acids of Solidifying Point 42·8° C., containing: Oleic Acid, 42·8 per cent.; Neutral Fat, 0·5 per cent.			
	Solidifying Point.	Oleic+Iso-oleic Acids.	Hydroxy-stearic Acid.	Hydrocarbons.	Solidifying Point.	Oleic+Iso-oleic Acids.	Hydroxy-stearic Acid.	Hydrocarbons.	Solidifying Point.	Oleic+Iso-oleic Acids.	Hydroxy-stearic Acid.	Hydrocarbons.
	°C.	Per cent.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	Per cent.
5	41·7	33·1	4·0	...	37·8	50·3	5·9	...	45·9	51·2	6·0	...
6	41·9	33·8	4·3	...	37·9	51·1	6·0	...	45·9	51·5	6·0	...
7	42·2	34·4	4·5	...	38·3	51·5	6·3	...	46·0	52·4	6·3	...
8	42·5	35·0	4·7	...	38·3	51·9	6·3	...	45·8	52·4	7·0	...
9	42·7	35·7	5·5	...	38·3	52·3	6·8	...	44·8	53·3	7·5	...
10	42·7	36·1	5·5	...	38·3	53·0	8·0	...	44·2	53·8	7·5	...
11	42·7	36·6	5·8	...	38·4	53·4	8·2	...	43·8	54·2	5·0	...
12	43·0	36·9	5·8	...	38·5	53·8	8·3	...	42·9	54·7	4·2	...
13	43·0	37·7	6·0	...	39·5	54·2	8·3	...	42·7	54·8	3·0	...
14	43·3	38·3	6·3	...	39·6	54·7	6·2	...	41·8	55·8	2·8	...
15	43·5	38·8	5·9	...	39·7	55·7	6·0	0·3	41·0	56·5	2·8	...
16	43·8	39·1	5·7	...	39·9	58·6	3·2	0·5	41·0	57·2	2·8	...
17	44·1	39·6	5·7	...	40·0	58·6	3·0	0·9	40·8	58·0	1·0	0·2
18	44·4	40·4	5·0	...	40·2	59·1	2·2	1·1	40·5	59·1	...	0·3
19	44·6	40·8	3·7	0·2	40·2	59·3	1·4	1·3	40·1	59·9	...	0·5
20	45·0	41·3	3·3	0·5	40·5	59·7	0·5	1·5	39·8	60·7	...	0·5
21	45·2	41·5	3·0	0·7	40·7	60·4	...	1·9	39·8	61·5	...	0·6
22	45·2	42·2	1·1	0·7	40·8	60·9	...	2·2	39·3	61·6	...	0·8
23	45·8	42·2	...	1·2	41·0	61·5	...	2·7	39·0	61·9	...	2·0
24	45·0	42·4	...	1·3	40·8	61·5	...	3·0	38·8	63·0	...	2·2
25	42·7	42·5	...	1·8	39·9	61·8	...	3·6	38·8	63·0	...	2·7

The "still-returns" of the "Tallow Acids" and "Bone Fat Acids" of table p. 236, and of Nos. 1, 2, 3 of the table given on preceding page, collected together and again distilled, gave the following result (*Kassler*[1]):—

Distillation of "Still-Returns"

Quantity distilled.	Duration of Distillation.	Distillate for Presses.	Second "Still-Returns" ("Green Oil").	Stearine Pitch.
Tons.	Hours.	Per cent.	Per cent.	Per cent.
2·5	23	77·2	17·0	5·8

The yield obtainable from neutral fats by the "mixed process" should therefore be:—

Yield from 100 parts of Tallow by the "Mixed Process"

Candle material	61-63 per cent
Oleic acid	32-30 ,,
Crude glycerin, specific gravity 1·240 . .	10-10 ,,
Pitch; Loss	2- 3 ,,

---

[1] *Chem. Revue*, 1902, 74.

Conversion of Oleic Acid into Candle Material[1]

It has been shown that in the "acid saponification process" about 30 per cent of oleic acid is obtained as a by-product. Ever since candle-making from "stearine" was introduced, numerous workers have endeavoured to convert oleic acid completely into a saturated acid, or at least into candle material.

The earliest attempts were directed to the reduction of oleic acid into *stearic acid*. It has been pointed out above (Vol. I. Chap. III.), that whereas the lower members of the oleic acid series can be converted into saturated acids by means of sodium amalgam in alkaline solution, oleic acid does not take up hydrogen under these conditions.

Oleic acid can be reduced to stearic acid by means of fuming hydriodic acid and phosphorus (Vol. I. Chap III.), but, viewed as the basis of a commercial process, this reaction must be looked upon as hopeless. By heating oleic acid with 1 per cent of iodine to 270°-280° C., *P. de Wilde and Reychler* succeeded in obtaining only about 70 per cent of stearic acid. Moreover, not more than one-third of the iodine used could be recovered; hence also this process had to be abandoned. Even when the iodine was partly or wholly substituted by the cheaper bromine or chlorine, commercial failure resulted. The process had a fair trial on a large scale in a Belgian candle-works, but the large amount of valueless by-products, coupled with the fact that no material from which the autoclaves were made could resist the corrosive effect of the halogens, showed once more that beautiful laboratory experiments but too often lead to unfavourable results in large-scale operations.

The action of chlorine on oleic acid, and the reduction of the chloro-derivatives under pressure by means of zinc or iron powder has been made the subject of a German patent by *Zürrer*, who claims to have obtained solid saturated fatty acids.[2] Since, however, oleic acid is regenerated on the reduction of monochlorostearic acid, as the author's laboratory experiments show, this process cannot be a feasible one. Indeed, as far as the author has been able to ascertain, this process has not been worked on a commercial scale.

The author has carried out a number of experiments in a similar direction with bromo-derivatives of stearic acid obtained by converting oleic acid into monobromostearic acid as also into dibromostearic acid, but on reducing the products by means of hydrogen no stearic acid was obtained.

The conversion of oleic acid into *palmitic acid*, as indicated by *Varrentrapp's* reaction (Vol. I. Chap. III.), has been repeatedly tried on a large scale; lastly by *Radisson* in *Fournier's* works at Marseilles.[3] Although candles made by this process were shown at the Paris Exhibition of 1878, they have disappeared from the market on account of their rank odour and their greasy touch. The writer ascertained[1] that the process was abandoned not only for the reasons stated, but also on account of the high cost and the great danger attending the process in consequence of the evolution of hydrogen. This method has again been proposed by *Schrauth*[2] for the preparation of soap-stock from crude fish oils.

---

[1] Cp. Lewkowitsch, "On Attempts to convert Oleic Acid into Candle Material, I." *Journ. Soc. Chem. Ind.*, 1897, 390; and "The Conversion of Oleic Acid into Candle Material, II." *ibid.*, 1908, 489.

[2] German patent 62,407 (1892).

[3] *Journ. Soc. Chem. Ind.*, 1883, 98; 1884, 200.

The conversion of oleic acid into *elaïdic acid* (Vol. I. Chap. III.), although frequently patented, does not lead to technically useful results. The conversion of oleic acid into elaïdic acid by means of nitrous acid is not complete, hence the purification of the crude elaïdic acid alone renders this process unremunerative. The change of oleic acid into elaïdic acid by means of sodium bisulphite is a reversible one, and therefore leads to a low yield of elaïdic acid. Moreover, elaïdic acid, even if pure, is not a good candle material.

The action of *zinc chloride* on oleic acid with a view to converting it into solid material has been tried, at temperatures of about 200° C., without commercial success. The study of the reaction was again taken up by *M. v. Schmidt.* 10 parts of oleic acid were heated with 1 part of zinc chloride to exactly 185° C., until a sample after being boiled with hydrochloric acid solidified on cooling. The resulting product was then repeatedly boiled out, first with hydrochloric acid, and finally with water. The crude product obtained by the interaction of zinc chloride and oleic acid had, according to *Benedikt*,[3] the following composition :—

	Per cent.
Liquid anhydrides	8
Stearolactone	28
Oleic and iso-oleic acids	40
β-Hydroxystearic acid (ι-hydroxystearic) . . .	22
Saturated fatty acids (by difference) . . .	2
	100

[In examining this process on a laboratory scale the author found no solid saturated acids other than hydroxystearic acid.[4] *Shukoff and Schestakoff* stated that they never obtained more than 8-9 per cent of stearolactone.[5]]

The crude product was distilled in a current of superheated steam, and the distillate separated by hydraulic pressure into candle material and oleic acid. The candle material thus prepared gave on analysis the following result :—

	Per cent.
Stearolactone	75·8
Iso-oleic acid	15·7
Solid fatty acids	8·5
	100·0

---

[1] Technical Report on the Paris Exhibition, *Chem. Zeit.*, 1889, 1190.

[2] *Zeits. f. angew. Chem.*, 1916, 29, ref. 31. Cp. also E. Bennecke, English patent 141,720, 1920.

[3] Benedikt, *Monatsh. f. Chem.*, 1890, 71 ; *Journ. Soc. Chem. Ind.*, 1890, 658.

[4] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1897, 392.

[5] *Journ. f. prakt. Chem.*, 1903 (67), 418.

M. v. Schmidt's process was tried on a large scale in an Austrian candle-works. The quantity of oleic acid that remained unattacked, and the considerable amount of liquid unsaponifiable substances formed was so great, that the process had to be abandoned.

Zinc chloride seems to act on oleic acid in a manner analogous to the action of concentrated sulphuric acid (cp. also "Polymerised Castor Oil," p. 141). Very likely two isomeric zinc chloride addition-compounds are formed, which are subsequently decomposed on boiling with dilute hydrochloric acid into zinc chloride and two isomeric hydroxystearic acids, one of which is changed into stearolactone with loss of one molecule of water.

Until recently the only process for the conversion of oleic acid into candle material, adopted in practice, rested on the interaction of sulphuric acid with oleic acid. *Geitel*[1] has shown that on dissolving oleic acid in cold concentrated sulphuric acid, stearic acid hydrogen sulphate is formed.[2] On subsequently boiling the product with water, ι-hydroxystearic acid and small quantities of stearolactone are obtained, and on distilling the mass in a current of steam, as is done on a large scale, the stearolactone passes over unchanged, whereas the ι-hydroxystearic acid is converted into oleic and iso-oleic acids. Besides, liquid anhydrides are formed. This play of (partly reversible) reactions explains why, on working the sulphuric acid saponification on a large scale, out of the 47 per cent of oleic acid obtainable from tallow in the autoclave process (p. 234), only 15-17 per cent is converted into candle material, 30 per cent of oleic acid still being obtained as a by-product.

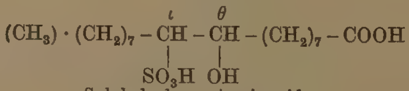
The rationale of the chemical action taking place when sulphuric acid acts on oleic acid in the cold may, perhaps, be explained as follows (*Lewkowitsch*[3]):—

In the first instance sulphuric acid is assimilated by oleic acid, much as bromine is absorbed by the latter, with the formation of saturated products. But in the present case there is this important difference, that since two different groups, SO_3H and OH, are absorbed, two products may be expected, according as to whether the SO_3H group is assimilated by the ι or the θ carbon atom, thus—

$$(CH_3)\cdot(CH_2)_7\cdot CH=CH-(CH_2)_7\cdot COOH$$

Oleic acid

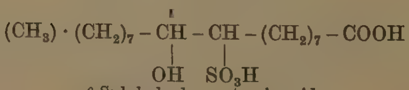
yields

(1) 

$$(CH_3)\cdot(CH_2)_7-\overset{\iota}{\underset{SO_3H}{CH}}-\overset{\theta}{\underset{OH}{CH}}-(CH_2)_7-COOH$$

ι-Sulphohydroxystearic acid

and

(2) 

$$(CH_3)\cdot(CH_2)_7-\overset{\iota}{\underset{OH}{CH}}-\underset{SO_3H}{CH}-(CH_2)_7-COOH$$

θ-Sulphohydroxystearic acid

---

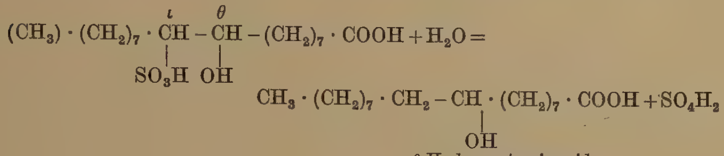
[1] Cp. Vol. I. Chap. III.

[2] Dubovitz (*Seifensieder Zeit.*, 1908, 729) suggests that some reactions of the compound may be best explained by the formula $C_{17}H_{34}(COOH)-SO_4-C_{17}H_{34}(COOH)$.

[3] Cp. *Journ. Soc. Chem. Ind.*, 1897, 392.

As there is no reason why the one acid should be formed in preference to the other, it may be assumed that both acids are formed in equal proportions.[1] These acids are not very stable, and by merely allowing the crude product to stand, enough moisture is absorbed to lead to a portion being split up into SO_4H_2 and hydroxylated acids. This may be explained by the following equations :—

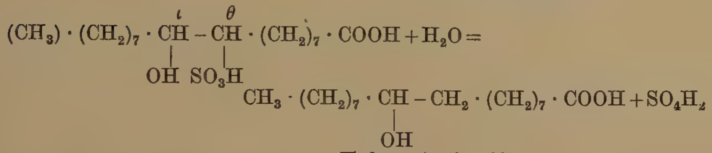
(1)



$$(CH_3)\cdot(CH_2)_7\cdot\underset{SO_3H}{\overset{\iota}{CH}}-\underset{OH}{\overset{\theta}{CH}}-(CH_2)_7\cdot COOH+H_2O=$$
$$CH_3\cdot(CH_2)_7\cdot CH_2-\underset{OH}{CH}\cdot(CH_2)_7\cdot COOH+SO_4H_2$$

θ-Hydroxystearic acid.

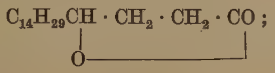
(2)



$$(CH_3)\cdot(CH_2)_7\cdot\underset{OH}{\overset{\iota}{CH}}-\underset{SO_3H}{\overset{\theta}{CH}}\cdot(CH_2)_7\cdot COOH+H_2O=$$
$$CH_3\cdot(CH_2)_7\cdot\underset{OH}{CH}-CH_2\cdot(CH_2)_7\cdot COOH+SO_4H_2$$

ι-Hydroxystearic acid.

The hydroxystearic acid termed here θ-hydroxystearic acid, immediately undergoes dehydration with the formation of a lactone which has been described hitherto as γ-stearolactone (Vol. I. Chap. III.). *Shukoff and Schestakoff* ascribe to this lactone the formula of a γ-lactone, thus—



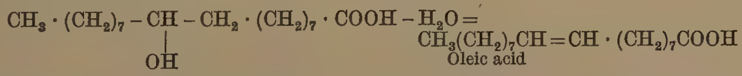
$$C_{14}H_{29}\underset{\lfloor O}{CH}\cdot CH_2\cdot CH_2\cdot \underset{\rfloor}{CO}\,;$$

hence a molecular rearrangement must be assumed to have taken place (cp. Vol. I. Chap. III.).

Another portion of the sulphohydroxystearic acid remains unchanged, but on boiling the crude mass with water the undecomposed portion also is converted into stearolactone and ι-hydroxystearic acid, as shown.

In the subsequent distillation of the washed product the stearolactone already formed passes over unchanged, together with part of the ι-hydroxystearic acid, whereas another part of the latter is dehydrated and, according as to whether the OH group takes up hydrogen from its right or left CH_2 group, is converted into oleic *and* iso-oleic acids, thus—

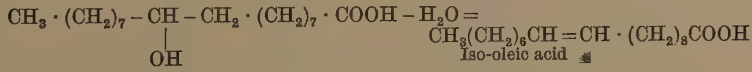
(1)



$$CH_3\cdot(CH_2)_7-\underset{OH}{CH}-CH_2\cdot(CH_2)_7\cdot COOH-H_2O=$$
$$CH_3(CH_2)_7CH=CH\cdot(CH_2)_7COOH$$

Oleic acid

(2)



$$CH_3\cdot(CH_2)_7-\underset{OH}{CH}-CH_2\cdot(CH_2)_7\cdot COOH-H_2O=$$
$$CH_3(CH_2)_6CH=CH\cdot(CH_2)_8COOH$$

Iso-oleic acid

Here, again, there is no reason why oleic and iso-oleic acids should not be formed in equal proportions. It is evident that unless distillation can be avoided, a complete conversion of oleic acid into solid products cannot be effected.

---

[1] On sulphonating oleic acid with concentrated sulphuric acid at 0° C. and treating the product of the reaction with water, 50 per cent of stearolactone is stated to be formed (David, *Compt. rend.*, 1897 (124), 466).

In the "acid saponification" process the interaction takes place at a high temperature, and it is therefore readily intelligible that, since the chemical changes involved are reversible, a limit is reached beyond which the proportion of converted oleic acid cannot be increased.

With a view to ascertaining how far the conversion into saturated products takes place, *Lewkowitsch*[1] examined the action of sulphuric acid of varying strengths on oleic acid, both on a laboratory and on a large scale. The results are given in the following table :—

Action of Sulphuric Acid of Varying Strength at 5° *C. on Oleic Acid of Iodine Value* 80 (*Lewkowitsch*)

Oleic Acid.	Sulphuric Acid.		Iodine Value of the Product.
Molecules.	Containing SO_4H_2.	Molecules.	
	Per cent.		
1	95	1	39·83
1	95	1	33·73
1	95	1	47·23
1	103 (fuming acid)	1	26·26
1	103 (fuming acid)	1	20·43
1	95	2	10·9
1	95	2	10·86
1	95	2	10·28
1	95	2	11·15
1	95	2	14·99
1	92	2	23·02
1	92	2	24·06
1	103 (fuming acid)	2	10·28
1	100·5 (mixture of fuming and concentrated acids)	2	14·40
1	100·5 (mixture of fuming and concentrated acids)	2	14·41
1	95	2·5	16·73
1	92·5	2·5	23·60
1	93	2·5	19·61
1	95	3	6·74
1	95	3	8·46
1	103 (fuming acid)	3	16·04

It will be seen that, contrary to expectation, the greatest amount of saturated products is not obtained when acid containing 100 and more per cent of SO_4H_2 is used. The crude products gave on examination the following results :—

---

[1] *Journ. Soc. Chem. Ind.*, 1897, 392.

Crude Product obtained by the Interaction of Sulphuric Acid and Oleic Acid at a Low Temperature (Lewkowitsch)

No.	Oleic Acid.	Sulphuric Acid.		Laboratory Experiments.			Works' Experiment.		
	Molecule.	Containing—Per cent SO_4H_2	Molecules.	Acid Value.	Saponification Value.	Iodine Value.	Acid Value.	Saponification Value.	Iodine Value.
1	1	95	1	157·8	179·2	31·8	98·4	198·3	24·8
2	1	100·5 (mixture of fuming and concentrated acids)	1	136·1	192·6	23·1	...	...	...
3	1	103 (fuming acid)	1	120·8	169·5	24·3	...	...	...

The crude product was distilled with superheated steam, and gave the numbers contained in the following table :—

Distillation of Crude Products with Superheated Steam (Lewkowitsch)

No.	Crude Product obtained from Oleic Acid and Sulphuric Acid containing—per cent SO_4H_2.	Laboratory Experiments.						Works Experiment.					
		First Fraction.	Second Fraction.	Third Fraction.	Fourth Fraction.	Residue.	Loss.	First Fraction.	Second Fraction.	Third Fraction.	Fourth Fraction.	Residue.	Loss.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
	1 Mol. of oleic acid and 1 Mol. of SO_4H_2 :—												
1	95	27·4	42·7	20·4	1·9	4·0	3·6	30·0	30·0	26·5	...	6·2	7·3[2]
2	100·5 (mixture of fuming and concentrated acids)	26·6	46·5	17·6	...	6·2	3·1	...	...	...	...	...	...
3	103 (fuming) . . .	19·5	16·9	33·7	14·9	11·7	3·3	...	...	...	...	...	...
	1 Mol. of oleic acid and 2 Mols. of SO_4H_2 :—												
4	93	11·0	13·8	12·2	52·7	6·5	3·8	...	...	...	...	...	...
5	96·5	9·5	11·9	13·6	51·5	6·6	6·9[1]	...	...	...	...	...	...

[1] The still leaked a little.

[2] This high loss is due to the exceptional circumstances under which the experiment was carried out.

The several fractions obtained from the crude products, Nos. 1, 2, and 3, gave the numbers stated in the following tables :—

Characteristics of the several Fractions of Crude Product No. 1

	Laboratory Experiment.				Works Experiment.			
	First Fraction.	Second Fraction.	Third Fraction.	Fourth Fraction.	First Fraction.	Second Fraction.	Third Fraction.	Bulk.
Iodine value .	58	84·3	83·8	82·4	82·8	85·2	65·8	77·1
Neutralisation value	192	196·5	196·9	188·1	197·5	197·3	194·1	197·5
Saponification value	201	201·2	199·9	194·9	200·7	200·0	188·9	201·3
Melting point, ° C.	Liquid	27·2-28·3	27·2-29	25·5-29	20·2	25·3	24·9	23·45

Characteristics of the several Fractions of Crude Product No. 2

	Laboratory Experiment.		
	First Fraction.	Second Fraction.	Third Fraction.
Iodine value . .	56·6	78·5	82·2
Neutralisation value .	197·6	198·2	194·6
Saponification value .	201·7	199·9	198·4
Melting point, ° C. .	Liquid	26·6-28·3	26·6-29

Characteristics of the several Fractions of Crude Product No. 3

	Laboratory Experiment.			
	First Fraction.	Second Fraction.	Third Fraction.	Fourth Fraction.
Iodine value . .	61·9	73·4	81·4	84·1
Neutralisation value .	204·5	200·5	198·9	192·8
Saponification value .	209·1	203·3	199·7	194·5
Melting point, ° C. .	Liquid	Liquid	26·1-27·2	29-29·4

It should be borne in mind that the iodine numbers correspond to a mixture of oleic and iso-oleic acids. The melting points of the products show that considerable quantities of iso-oleic acid have been formed. The small differences between the saponification and the neutralisation values prove that stearolactone is present in small quantities only

David's[1] statement that 18-20 per cent of stearolactone is formed in the cold by washing the product of interaction of oleic and sulphuric acids with an equal volume of water, removing the acid layer, dissolving the oily layer in an equal volume of water, and allowing to stand for twelve hours, has been shown by *Lewkowitsch*[1] to be erroneous, for the separated crystals were practically nothing else but ι-hydroxystearic acid.

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[1] *Journ. Soc. Chem. Ind.*, 1897, 339. Cp. French patent 252,263.

Lewkowitsch's stricture has been confirmed later on by *Shukoff*.[2]

Experiments made with a view to simulating the conditions which obtain in practice in the acid saponification process, by allowing sulphuric acid to interact with oleic acid at 132° C., and by subsequently distilling, are detailed in the following tables :—

Product obtained by the Interaction of Sulphuric Acid and Oleic Acid at 132° *C. and subsequent distillation.* (*Works Experiment.*) (*Lewkowitsch.*)

	Iodine Value.	Neutralisation Value.	Saponification Value.	Melting Point.
				°C.
Crude product	53·90	169·8	...	...
Bulk distillate from crude product	71·60	180·2	202·0	20·70
Bulk distillate :—				
Cold-pressed cake . . .	69·45	195·5	207·8	30·80
,, oil . . .	72·10	184·8	202·2	Liquid
Hot-pressed cake . . .	...	202·8	206·7	43·05 (Titer test)

Product obtained by the Interaction of Sulphuric Acid and Oleic Acid at 132° *C. and subsequent distillation.* (*Laboratory Experiment.*) (*Lewkowitsch.*)

	Yield.	Neutralisation Value	Saponification Value.	Melting Point.
	Per cent.			°C.
First fraction .	10·8	181·16	201·3	Liquid
Second ,, .	39·0	167·38	193·9	25·5-30
Third ,, .	16·6	152·68	191·9	25·5-32
Residue . .	29·4	...	...	...
Loss . .	4·2	...	...	...

Although the proportion of stearolactone in these products is higher than in the crude products described in tables pp. 250 and 251, still, the results set out in the last two tables prove that the interaction of sulphuric acid with oleic acid at high temperatures cannot lead to a technically valuable process.

Finally, the author gives the results of an experimental distillation of a crude product, obtained by the interaction of one molecule each of oleic acid and of sulphuric acid containing 95 per cent SO_4H_2, after freeing it from hydroxystearic acid.

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[1] *Journ. Soc. Chem. Ind.*, 1897, 390.

[2] French patent 328,604; German patent 150,798.

Distillation of Crude Product freed from Hydroxystearic Acid (Lewkowitsch)

	Yield.		Melting Point.	
	I.	II.	I.	II.
	Per cent.	Per cent.	°C.	°C.
First fraction .	24·0	23·4	Liquid	Liquid
Second ,, .	24·0	29·2	24-29	Oily
Third ,, .	32·9	13·9	24·4-29·4	24·4-27·7
Fourth ,, .	7·8	22·9	20·0-25·5	26·6-30·5
Residue . .	5·1	5·7	...	...
Loss . .	6·2	4·9	...	...

The considerable amount of liquid products obtained must not be looked upon as consisting entirely of unchanged oleic acid. These liquid substances contain anhydrides, or polymerisation products.

Hausamann[1] acidifies the mixed fatty acids, obtained in an autoclave in the usual manner, at an elevated temperature with concentrated sulphuric acid, after which the mass is distilled. The distillate is cooled till the mass has solidified completely, and is then treated once more with sulphuric acid in the cold. The example which the inventor gives is not very encouraging, as the second treatment only raises the titer test of the once acidified fatty acids from 40° C. to 43·5-44° C. Moreover, he himself declares that it is impossible to convert the total quantity of the oleic acid into solid material. This is, of course, due to the formation of anhydrides.

K. Hartl[2] endeavoured to avoid the drawback inherent to the process of distilling the acidified mass (see above, p. 245, and below) by purifying oleic acid (or the mixed fatty acids) by distillation and by treating the distillates subsequently with concentrated sulphuric acid. As *Lewkowitsch* has pointed out elsewhere,[3] it is difficult to see any novelty or advantage in this method. Shortly afterwards *Hartl's* patent was cancelled.

A. A. Shukoff[4] avoids temperatures exceeding 100° C. in the acidifying process, and aims at the direct production of stearolactone, by acidifying with the theoretical amount of concentrated sulphuric acid of 64° Bé. at temperatures lying between 70° and 80° C. The reaction requires from seven to twelve hours for completion. The final product which the author had occasion to examine was perfectly white and hard; it was practically pure stearolactone, for its acid value was *nil*; its saponification value was 199·3, and its iodine value

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[1] French patent 335,768, 1903.

[2] German patent 148,062 (1903).

[3] *Jahrbuch d. Chem.*, 1903, xiii. 414.

[4] French patent 328,604 (1903); German patent 150,798. Cp. also Vol. I. Chap. III. "Oleic Acid."

1·1. An intermediate product, requiring further purification, had the following characteristics (*Lewkowitsch*) :—

Titer test	26·7° C.
Acid value	153·9
Saponification value	194·3
Iodine value	55·17

Of course, the conversion of oleic acid into the solid product is not complete. The inventor states that the yield of candle material is satisfactory. As far as the author is aware, this process has not been taken up by other manufacturers. It is noteworthy that the melting points of mixtures of the lactone with paraffin wax are the arithmetical means of the melting points of the two components.

The patent specifications of *Dreymann*[1] offer no novelty as regards the acidification and increased yield of candle material. It need, therefore, only be mentioned that the patentee adds before distillation an oxide or carbonate to the acidified and washed mass, in order to neutralise any sulphuric acid left in it.

P. Wunder[2] combines, as it were, the acid saponification process with the process described under (1), by acidifying fats with 5 to 15 per cent of sulphuric acid of 66° Bé. whilst a current of superheated steam, at 150° C., is passed through the mixture. The oleic acid pressed off, the saponified mass is re-introduced into the process, and the inventor claims thus to obtain 85 to 90 per cent of solid fatty acids. Whilst the re-working of the oleic acid can hardly be considered a novelty, the high yield of solid fatty acids must be open to grave doubts.

Lewkowitsch[3] suggested, as a practical working method, to remove from the acidified mass, after treatment with water, the hydroxystearic acid formed thereby, since during distillation of the acidified mass hydroxystearic acid is broken down to a mixture of oleic and iso-oleic acids. The large-scale experiments were, however, not continued for a sufficient length of time, to arrive at definite results. The work was taken up later on by the *Standard Oil Company* of Whiting, near Chicago, and led to a process of making hydroxystearic acid from oleic acid.[4] The *modus operandi* is as follows :—Oleic acid is dissolved in light petroleum ether (1 volume of acid and 2 volumes of petroleum) and is then treated with sulphuric acid. The process is carried out at the low temperature of 40° F., hence the chemical reaction is easily controlled, and the injurious influence of a rise of temperature is more easily prevented than when oleic acid alone is employed. The acidified mass is treated with steam so as to obtain hydroxystearic acid. Thus 50 per cent of the oleic acid is stated to become converted into hydroxystearic acid. On cooling the solution the hydroxystearic acid separates in the crystalline form ; the crystals are filtered and dried in a centrifugal machine, and are then ready for use. By driving off the solvent from the filtrate, unattacked oleic acid and stearolactone are recovered; they are then purified by distillation, and again subjected to the same treatment with sulphuric acid. The yield of hydroxystearic acid is stated to be 85 to 90 per cent. The melting point of the hydroxystearic acid is higher than that of stearic acid, but this property alone does not yet prove that the former is suitable for candle-making. This is borne out by a statement made in a later specification,[1] viz. that hydroxystearic acid, when mixed with paraffin wax in as low a proportion as 15 to 25 per cent, does not furnish saleable candles, inasmuch as it causes "stratification" in the moulded candle, and tends to accumulate at the extremities of the candle. The seriousness of this drawback will be better understood, if it be remembered that, in the manufacture of composite candles, stearic acid can be admixed with paraffin wax in any proportion from 5 per cent upwards. Therefore, a mixture of 3 parts of hydroxystearic acid with 1 part of commercial stearic acid is recommended as a stock mixture for "stiffening" paraffin wax candles. Provided the results claimed by the specifications are obtained regularly on a large scale, this method would represent the most advantageous form of the *sulphuric acid process.*

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[1] English patent 19,988, 1905 ; French patent 358,212 ; German patent 166,610.

[2] German patent 116,695, 1895.

[3] *Journ. Soc. Chem. Ind.*, 1897, 393.

[4] United States patent 772,129, W. M. Burton, Assignor to the Standard Oil Company, 11th October 1904 ; English patent 20,474, 1904 ; French patent 348,089.

A claim made by *Tissier* [2] to have effected a (partial) conversion of oleic acid into stearic acid by means of hydrogen, evolved whilst saponifying fats in an autoclave with zinc and zinc dust (by the action of the latter on water), hardly required refutation. Still, *Freundlich and Rosauer* [3] have shown, by experimenting with oleic acid and bone fat in an autoclave, that oleic acid was not reduced to stearic acid. Possibly *Tissier's* error is best explained by the formation of zinc soaps, which naturally raise the melting point of the oleic acid in which they are dissolved.[4] It may be recalled here that *Lewkowitsch* was not able to effect a reduction of oleic acid by hydrogen *in statu nascendi.*[5]

A kind of connecting link between the sulphuric acid processes and the processes invoking the aid of electricity (see below) is exemplified by the patents of *Magnier, Bragnier, and Tissier.*[6] The acidification is carried out in the usual manner, whereupon the acidified mass is mixed with five to six times its weight of water, and is then subjected to the action of an electric current (under a pressure of 5 atmospheres). It appears to the author extremely doubtful whether any larger yield of candle material is obtained than by the sulphuric acid alone, *i.e.* without the electric current. Confirmation of the author's opinion may be found in the fact that this process has not found its way into practice.

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[1] United States patent 802,100, G. R. Gray, Assignor to the Standard Oil Company; English patent 17,945, 1905; French patent 357,507; German patent 174,471 (cp. also below).

[2] *Russian Privilegium,* 1499, of January 1897.

[3] *Chem. Zeit.,* 1900, 566.

[4] The same error appears to have misled *A. Knorre,* who claims (German patent 172,690) the conversion of oleic acid into solid fatty acids by treatment with formaldehyde in the presence of finely divided metals (zinc); cp. Halpern, *Chem. Zeit.,* 1907, 845.

[5] *Journ. Soc. Chem. Ind.,* 1897, 390.

[6] English patent 3363, 1900; French patent 291,839; German patent 126,446; additional German patent 132,223.

A process attempting to effect the conversion of oleic acid into stearic acid by electrical discharges in an atmosphere of hydrogen has been patented by *A. de Hemptinne.*[1] The electrical discharges are produced between a number of metal plates (separated by glass plates so as to prevent short-circuiting between the metal plates) which are alternately connected with the poles of a generator of electrical energy. Oleic acid is allowed to trickle in a fine stream (by sprinkling arrangement) on to the plates enclosed in a vessel through which hydrogen passes [2] at a pressure below that of the atmosphere. By rotating the apparatus slowly the oleic acid forms a moving film, thus continually exposing a fresh surface to the hydrogen. *A. de Hemptinne* states [3] that 50 per cent of oleic acid is converted into stearic acid. According to the English patent specification, the process is interrupted when about 20 to 30 per cent of stearic acid is formed. The mass is then withdrawn, cooled, and the filtrate again treated as before, until the accumulation of by-products prevents the further formation of stearic acid. This process deserves the attention of the candle-maker, and would recommend itself on account of its simplicity, provided a much higher yield of stearic acid could be reached through inhibiting the formation of condensation products and of resinous substances.

J. Petersen [4] also endeavoured to reduce oleic acid to stearic acid by allowing an electric current to act on an alcoholic oleic acid solution, slightly acidulated with sulphuric acid (or preferably with hydrochloric acid), between nickel electrodes. But the yield of stearic acid was small; even under the most favourable conditions it did not exceed 15 to 20 per cent. When platinum electrodes were employed no reduction at all took place. Hence, so far this process cannot claim the attention of the candle manufacturer.

C. F. Böhringer und Söhne [5] obtained by the same method much better results when using as cathodes metallic electrodes, which were covered with a spongy layer of the same metal. They recommend as cathodes platinised platinum, and also palladium electrodes covered with a spongy layer of palladium-black. Nickel electrodes covered with spongy nickel may also be used, but in this case, with a current density of 100 ampères per square meter, only a "considerable reduction" is stated to have taken place. If copper be substituted for nickel, and the current density be reduced to 10 ampères per square meter, slight reduction only was noticed. The following details are given by the patentees :—25 volumes of oleic acid or erucic acid (or their methyl-esters) were dissolved in 250 volumes of strong alcohol, and 5 to 10 volumes of 30 per cent sulphuric acid or of a 20 per cent hydrochloric acid solution were added. When employing a platinised platinum cathode, and electrolysing with a current density of about 1 ampère per square meter at a voltage of 4 to 6, the temperature being kept between

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[1] English patents 1572, 12,525, 1905; French patents 349,942, 350,955, 363,078; German patents 167,107, 169,410; United States patent 797,112.

[2] The apparatus is illustrated in English patent 7101, 1905.

[3] *Bull. de l'Acad. royale de Belgique*, 1904 (5), 550; cp. also *Bull. Soc. chim. de Belgique*, 1912, 55.

[4] *Zeits. f. Elektrochem.*, 1905, 549.

[5] German patents 187,788, 189,332 (1906).

20° and 50° C., the " whole of the oleic acid " was stated to be reduced to stearic acid after 7 ampère-hours per kilo of oleic acid had been used. In the case of a palladium electrode covered with palladium-black at a current density of 100-500 ampères per square meter, " the " (whole ?) oleic acid was reduced after 300 ampère-hours per kilo of material had been consumed, whilst stearic acid and ethyl stearate separated. Finally, in the case of a nickel cathode covered with a spongy layer of nickel and at the same current density, about one-third of the oleic acid was converted into stearic acid after 300 ampère-hours per kilo of acid had been consumed. *Waser* patents the electrolysis of the product obtained by the interaction of oleic acid with sulphuric acid.

In a survey of the modern work on the reduction of unsaturated acids, *Fokin*[1] states that the reduction of oleic acid can only be effected with the aid of cathodes of palladium, platinum, rhodium, iridium, osmium, nickel, cobalt, and copper. The best results were obtained by electrolytic reduction ; next as regards efficiency came reduction in the gaseous state in the presence of these metals, they acting as catalysts. Less favourable still were the yields with galvanic couples, and the lowest yields were obtained with metal hydrides. In all cases the reduction is ascribed to the activity of occluded hydrogen.

The above given practical data by *A. de Hemptinne*, *Petersen*, and *Boehringer* as to yields of stearic acid, taken in conjunction with the statements to be made below, do not bear out the correctness of *Fokin's* opinion that electrolytic reduction-processes furnish the highest yields. *Fokin's* error may be caused through his taking the rise of the melting point alone as a proof of the presence of stearic acid. Experiments which the author carried out several years ago on the reduction of oleic acid by means of hydrogen in the presence of catalysts[2] showed that the melting point is affected considerably, even by small quantities of metallic soaps—the last traces of which can only be removed with great difficulty. Although *Fokin* distinctly states that the presence of nickel soap caused him great difficulties, so that he must have been well acquainted with this source of error, his statements should nevertheless be accepted with reserve, until in each case stearic acid free from metal has been isolated.

The classical work of *Sabatier and Senderens* on the reduction of organic substances in the presence of finely divided metals, especially of finely divided nickel, was destined to create a new epoch in the solution of the present problem. Very shortly after the publication of *Sabatier and Senderens'* earlier work, and based upon it, a patent was taken out by the *Herforder Maschinenfett- und Ölfabrik, Leprince and Siveke*, for the conversion of unsaturated fatty acids or their glycerides into saturated compounds.[3]

The author had then already undertaken laboratory experiments on the lines of *Sabatier and Senderens'* work, but could not find that conversion of oleic acid into stearic acid had taken place to any notable extent. In the light of his present experience he can only account for his failure at that time by assuming that the conditions under which he then worked precluded the formation of stearic acid; or, in other words, that the contact-mass had been "poisoned." Immense amounts of oils, principally fish oils, are now being "hardened" by hydrogen in the presence of metallic catalysts (cp. p. 119).

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[1] *Zeits f. Elektrochem.*, 1906 (12), 749.

[2] Lewkowitsch, *Jahrbuch d. Chem.*, 1906, xvi. 400.

[3] German patent 141,029 ; English patent 1515, 1903, in the name of W. Normann.

Bedford[1] applied *Sabatier and Senderens'* method to the reduction of oleic acid to stearic acid (as also of ethyl crotonate to ethyl butyrate, and of ethyl linolenate to ethyl stearate), and, in conjunction with *Williams*,[2] describes, amongst other examples, the reduction of linseed oil to a solid substance, and of oleic acid to stearic acid, by using nickel as a contact substance. A German patent by *P. Schwoerer*[3] claims an apparatus for the conversion of oleic acid into stearic acid by the contact process. *Ipatiew*[4] obtained, by treating sodium oleate with hydrogen in the presence of copper oxide, "stearic acid," melting from 64°-67° C. The yield of solid acid has not been stated.[5]

The author, who had meanwhile resumed his earlier work on the reduction of oleic acid, succeeded by a systematic study[6] of *Sabatier's* reaction in converting oleic acid with a practically theoretical yield into stearic acid. As this result is of technical importance, reserve must be exercised with regard to the details of the method.

(5) SAPONIFICATION BY MEANS OF SULPHO-COMPOUNDS

The reagent employed in this process is obtained by allowing an excess of sulphuric acid to act on a solution of oleic acid in aromatic hydrocarbons. The product obtained, in case benzene is chosen as the aromatic hydrocarbon, has been described by *Twitchell* as having the composition $C_6H_4(SO_3H)(C_{18}H_{35}O_2)$.[7]

The composition of the reagent as actually supplied to the licensees under the name of "saponifier" is kept secret. The author does not therefore feel justified in making detailed statements as to the manner in which it is prepared for manufacturing purposes beyond pointing out that the aromatic hydrocarbon in the "saponifier" is naphthalene. The naphthalene has been replaced by cymene, which it is claimed increases the speed of hydrolysis.[8] *Petroff* patents the production of hydrolysing reagents by sulphonating naphthenic acids.[9]

The use of reagents prepared by sulphonating paraffin and tar oils has been patented.[10]

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[1] *Inaug. Dissert.*, "On the unsaturated acids of linseed oil and their quantitative reduction to stearic acid," Halle a/S., November 1906.

[2] English patent 2520, 1907, "Improvements in and relating to the reduction of organic substances."

[3] German patent 199,909; United States patent 902,177.

[4] *Berichte*, 1909, 2089.

[5] Cp. Erdmann, German patent 211,669; Sabatier, French patent 394,957; Skita and Paal, German patent 230,724.

[6] *Journ. Soc. Chem. Ind.*, 1908, 489; *Jahrbuch d. Chem.*, 1907, xvii. 415.

[7] *Journ. Amer. Chem. Soc.*, 1899, 22.

[8] R. H. M'Kee and L. J. Lewis, *Chem. and Met. Eng.*, 1921 (24), 969.

[9] Belgian patent 259,934; United States patent 1,079,437.

[10] Kontakt and G. Petroff, English patent 17,148, 1914. Cp. also R. E. Divine, United States patent 1,319,027, 1919.

The rationale of this process[1] is not yet fully understood. *Lewkowitsch* explains the action of the reagent (Vol. I. Chap. II.) by its power of emulsifying the glycerides. Several tables illustrating the action of three "*Twitchell* reagents" on oils and fats are given in Vol. I. Chap. II. The author may perhaps express the opinion that during the steaming of the fats and oils with the "*Twitchell* reagent" sulphuric acid is generated, as it were, *in statu nascendi*, and this acts on the glycerides with the formation of sulpho-compounds, which are more readily hydrolysed by water than are the glycerides themselves. The process differs, however, most essentially from the "acid saponification process," in that oleic acid is not simultaneously converted into solid material; hence the fatty acids obtained by this process have the same composition as those yielded by the autoclave process, as no sulpho acids can be formed, the sulphuric acid being too dilute to react with the oleic acid. For the abnormal behaviour of castor oil, the fatty acids of which form condensation products, see *R. O. Jones*.[2]

In the presence of a large excess of glycerin the process is a reversible one, triglycerides being formed from free fatty acids and glycerin. This reaction has been applied and patented[3] for the removal of the free fatty acids concomitant with rancidity in oils and fats. It is essential that the water formed in the reaction is removed and for this reason the process must be carried out either *in vacuo* or in a current of an inert gas.

It is essential that the fatty raw material be freed from impurities, such as lime, iron, as also from foreign organic substances. This is done by boiling the fat with a dilute solution of sulphuric acid in a manner similar to that employed in the purification of bone fat (Vol. II. p. 758). The purified fat is then transferred to wooden vessels furnished with perforated brass coils, and provided with well-fitting lids, which allow the steam to escape but prevent free access of air, since the fatty acids formed in this process readily darken on coming into contact with air. In these vessels the fat is mixed with 50 per cent of its weight of distilled water, 1·5 to 2 per cent (larger quantities cause very persistent emulsion and increase the tendency to discoloration) of the reagent are then added, and the whole mass is agitated by open steam passing through the perforated coil. It is essential that the fatty matter contain at the outset a small proportion of free fatty acids, as an entirely neutral fat requires a somewhat lengthy time before hydrolysis commences. This is no doubt due to the fact that the aqueous solution of the reagent requires the presence of fatty acids, in order to produce an emulsion which is essential for the progress of hydrolysis. With neutral fats a somewhat longer time is required to start the hydrolysis, as free fatty acids must be produced first by the boiling with water. But even at best the process requires a considerable time for the practical completion of hydrolysis, as is evidenced by the tables given, Vol. I. Chap. II. As an accelerator the use of colloidal clay has been proposed.[1]

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[1] English patent 4741, 1898; United States patent 628,503; German patent 114,491; French patent 456,956; English patent 9160, 1913; United States patent 1,082,622; Belgian patent 255,977. Cp. also Reuter, United States patent 1,068,079; Belgian patent 256,373; English patent 9160, 1913. E. Hoyer, *Chem. Zentr.*, 1921 (92), ii. 665; E. Twitchell, *Journ. Ind. and Eng. Chem.*, 1917, 194; A. C. Langmuir, *ibid.*, 1917, 195.

[2] *Journ. Soc. Chem. Ind.*, 1917, 359.

[3] *Verein. Chem. Werke*, A.G. French patent 454,315.

The progress of hydrolysis is controlled in the usual manner by determining the acid values of the product. For the purposes of the candle-maker it is essential that the hydrolysis be as complete as possible ; practically complete hydrolysis can be reached by prolonged boiling. The emulsion is then " broken " by the addition of sulphuric acid of 60° Bé., and the contents of the vessels are allowed to settle, when separation into two layers takes place—an upper layer of fatty acids, and a lower aqueous one containing glycerol. The fatty acids are drawn off and washed, and are ready for subsequent treatment.

The product is too dark to be made into candle material by pressing, which is feasible with autoclaved material. It is therefore imperative to distil the acids ; it commends itself to treat the fatty material, previous to distillation, with concentrated sulphuric acid, as described under process (3), so as to increase the yield of candle material. (Hence, strictly speaking, *Twitchell's* process, if applied to the production of candle material, would fall under the heading " Mixed Process.")

The *Twitchell* process lends itself most advantageously to raw material of low quality and rich in fatty acids, such as " greases," which cannot be worked up economically by autoclaving.

The yield from the *Twitchell* process is the same as that from the autoclave or from the mixed process, according to the manner in which the saponified material is treated, except in the case of coconut and palm-kernel oils, where a notable amount of volatile acids is carried away with the steam during the prolonged time of steaming with the reagent.

The foregoing processes yield as the chief product solid candle material (see below). The main by-products are *Oleic acid* and *Glycerin*, which are worked up by methods described below. Of less importance is the resulting " Stearine Pitch."

Stearine Pitch.—Candle Tar (French—*Goudron* ; German—*Stearinpech, Kerzenteer*) is the residue left in the stills (see p. 238). The pitch is run out from the bottom of the still whilst yet hot. According to the consistence, which depends on the treatment the " first run " residue has undergone and on the amount of volatile matter left in the residue, either a " soft pitch " or " hard pitch " is obtained. Soft pitch is easily soluble in benzene, carbonbisulphide, carbontetrachloride and other fat solvents ; on heating to 250°-350° C. it is converted into a hard, yet flexible mass, which is no longer soluble in the above-mentioned solvents. The employment of the hard substance as an insulating (covering) material has been patented by *Vogelsang*.[2] The " hard pitch " which is insoluble in the above solvents cannot be converted by heating into the flexible substance obtainable from the "soft pitch." The "soft pitch" is frequently used as a lubricant for heavy steel plate rollers—"hot neck grease." The "hard pitch" is employed for caulking ships' decks, as an insulating material for cables and electrical apparatus,[1] for waterproofing roofs and paper,[2] for making black varnishes[3] and anti-rusting paints.[4] *P. Lacallonge*[5] claims the manufacture of an ebonite-like mass obtained by mixing 80-90 per cent of stearine pitch with 10-20 per cent of ceresin, to which some picric acid has been added. A specially suitable material for insulating purposes (also for anti-corrosive paints) is said to be obtained by heating stearine pitch with sulphur at temperatures from 120° to 175° C.[6]

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[1] F. E. Weston, *Chem. Age*, 1921 (4), 604, 638 ; and also P. J. Fryer and Catalpo, Ltd., English patent 166,971, 1920.

[2] German patent 217,026.

Stearine pitch contains chiefly hydrocarbons, due to destructive distillation; and small quantities of free fatty acids and of neutral fat—together about 10 per cent. The definite acid and saponification values (as also evolution of acroleïn vapours) of stearine pitch permit of its being readily distinguished from petroleum residue (petroleum pitch) and lignite tar residue (brown-coal pitch).[7]

The presence of neutral fat in stearine pitch differentiates it from the cotton stearine pitch and wool grease pitch (Chap. XVI.), which are used for similar purposes.[8] For the determination of the saponification value *Marcusson*[9] recommends to dissolve 5 grms. of the pitch in 25 c.c. of benzin free from thiophene and boil the solution for one hour under a reflux condenser with 25 c.c. of normal alcoholic potash. After cooling, 200 c.c. of 96 per cent alcohol are added, and the solution titrated with hydrochloric acid, using phenolphthalein and alkali blue 6 B as indicators. The combination of these two indicators is stated to give a sharper end reaction than either used alone.[10]

For a method of determining the melting point of pitches by noting the temperature at which the ground pitch agglomerates in an electrically heated dilute solution of sulphuric acid the original paper should be consulted.[11]

The composition of some pitches obtained from fatty acids due to *H. Langton*[12] may be given here :—

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[1] Cp. also French patent 385,805 (Dupré and Icard).

[2] German patent 122,893.

[3] Cp. English patent 3345, 1906 (Connolly).

[4] E. Hildt, French patent 383,952.

[5] German patent 168,048.

[6] English patent 3045, 1894; cp. also Swedish patent 16,701, 1902 (Alexanderson and Ohlsson). Cp. also Wool Grease Pitch, p. 460.

[7] Cp. *Jahrbuch d. Chem.*, 1907, xvi. 414; and J. Marcusson, *Z. angew. Chem.*, 1918 (31), 113, 119.

[8] Cp. Holde and Marcusson, *Berichte*, 1900, 3173; Donath and Margosches, *Chem. Revue*, 1904, 194; 1905 (42), 73.

[9] Cp. W. Mansbridge, *Journ. Soc. Chem. Ind.*, 1918, 182 T.

[10] Marcusson, *Zeits. f. angew. Chem.*, 1911, 1299.

[11] French, *Journ. Ind. Eng. Chem.*, 1911, 907. Cp. also P. Spielmann and G. Campbell Petrie, *Journ. Soc. Chem. Ind.*, 1919, 68 T.

[12] *Journ. Oil and Colour Chemists' Association*, 1919, No. 7.

From Whale Oil Fatty Acids

	A	B
Consistence	Sticky	Hard and slightly brittle
Melting point	37·9° C.	68·5° C.
Specific gravity	1·016	1·046
Free fatty acids as oleic acid	10·7 per cent	5·41 per cent
Saponification value	67·8	104
Iodine value	126	97·9

Ultimate Analysis

	A	B
Carbon	77·11 per cent	73·19 per cent
Hydrogen	10·35 ,,	10·49 ,,
Nitrogen	Trace	Nil
Sulphur	Nil	Nil
Oxgyen by difference	12·06 per cent	9·09 per cent
Ash	0·48 ,,	7·23 ,,

From Palm Oil Fatty Acids

	A	B
Consistence	Soft	Hard and brittle
Melting point	43° C.	60·7° C.
Specific gravity	982	1·060
Free fatty acids as oleic acid	8·7 per cent	7·4 per cent
Saponification value	58·3	93·4
Iodine value	118·5	94·3

Ultimate Analysis

	A	B
Carbon	79·60 per cent	76·80 per cent
Hydrogen	11·26 ,,	9·28 ,,
Oxygen by difference	6·16 ,,	10·62 ,,
Ash	2·98 ,,	3·30 ,,

According as to whether the candle material prepared by the processes described above is used in the manufacture of candles alone, or is admixed with mineral waxes, we differentiate (*a*) stearine candles, or (*b*) mixed stearine and mineral wax candles.

The once flourishing tallow candle industry [1] has almost completely succumbed owing to the competition of the stearine and paraffin candles. The "tallow dip" candle has, therefore, but an insignificant local importance, although in this country alone about 1000 tons are still manufactured per annum. Tallow candles are, as a rule, not adulterated. Their commercial examination is identical with that of tallow (Vol. II. p. 764).

Candles made from spermaceti (sperm candles) and from beeswax (wax candles) will be described below under "Technology of Waxes."

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[1] It may be interesting to note that, as the Dominican monk Flamma reports, in the beginning of the thirteenth century tallow candles were still considered a luxury.

(*a*) Stearine Candles

The "stearine," "saponification stearine," "commercial stearic acid," obtained by the processes described under (1) and (2), consists practically of a mixture of stearic and palmitic acids.

The valuation of this material (as has been pointed out incidentally already) is based on its melting and solidifying points. The higher these are, the more valuable is the material. A definite iodine value indicates the amount of oleic acid left in the press cakes; a definite difference between the neutralisation and the saponification value corresponds to neutral fat that has escaped hydrolysis, and has not been pressed out with the oleic acid.

For commercial purposes it is but rarely required to ascertain the proportion of palmitic and stearic acids. If the direct determination of the stearic acid (Vol. I. Chap. VIII.) be too troublesome, the candle material may be valued (with sufficient accuracy for commercial purposes) on the basis of its solidifying points (cp. table, Vol. I. Chap. III. "Mixtures of Palmitic and Stearic Acids") and of the neutralisation value (cp. table, Vol. I. Chap. XII. "Neutralisation Values of Mixed Stearic and Palmitic Acids").

The "stearine" derived from the processes described under (3), (4), and (5) is also known as "commercial stearic acid." It is more correctly described as "distillation stearine." This is also valued on the basis of its melting and solidifying points. These are usually lower than those of the "saponification stearine," on account of their containing notable proportions of iso-oleic acid. The iodine value of a "distillation stearine" furnishes a measure of the amount of "iso-oleic" acid present; and the difference between the neutralisation and saponification values is a measure of the amount of lactone present. If the amount of hydroxystearic acid be required, the acetyl value must be determined. A complete analysis of "distillation stearine" embraces the determination of the iodine value, of the neutralisation and saponification values, of the acetyl value, and the direct estimation of stearic acid; palmitic acid is then found by difference.

By means of the iodine value it is possible to differentiate "saponification stearine" from "distillation stearine." The iodine value of the former rarely exceeds a few units, whereas "distillation stearine" gives iodine values varying, as a rule, between 15 and 30.

A considerable amount of neutral fat is contained in candle material intended for those composite candles (chiefly used for night-lights) which consist of a mixture of "stearine" and "coconut stearine." If an accurate determination of the neutral fat be desired, the safest plan is to saponify 50 grms. of the sample, and to determine the amount of glycerol.

The amount of unsaponifiable matter should be negligible. Notable amounts would point to admixture with hydrocarbons (paraffin wax, ceresin), black grease stearine, distilled grease stearine, and also carnaüba wax, which is sometimes admixed as a "candle hardener" to raise the solidifying point of the candle material. The examination of the isolated unsaponifiable matter is carried out by the methods given in Vol. I. Chap. IX. In this manner paraffin wax and ceresin, as also carnaüba wax, can be readily detected. The presence of iso-cholesterol points to admixture with "distilled grease stearine" (cp. Chap. XVI., and Vol. I. Chap. XI.). The amount of ash should be practically *nil.* It is important to determine the ash, as a definite amount, even 0·01 per cent, may lead to guttering of the finished candle.

Neutral fat (coconut oil) is sometimes added to prevent crystallisation if paraffin wax alone does not effect this satisfactorily.

The examination of the ash for lime and its quantitative determination is also required, as even very small quantities of lime left in the candle material cause the wick to yield a skeleton, which does not melt and drop off, but ultimately hangs down into the candle material and causes guttering. *Graefe*[1] showed that even as small a quantity as ·00075 per cent of lime (CaO) in the candle material is apt materially to injure the quality of an otherwise well-prepared wick. Ten times that quantity of lime—viz. ·0075 per cent—in a candle material would render the candles prepared from it unsaleable.[2]

The stearines obtained from greases generally contain notable amounts of unsaponifiable matter. The stearine from "black grease" (see Chap. XVI.) and other waste fats are also characterised by high amounts of unsaponifiable matter (cp. "Waste Fats," Chap. XVI.).

Candles consisting of "stearine" only are chiefly used in tropical or semi-tropical countries, where candles made from a mixture of stearine and paraffin wax would bend and gutter owing to their low melting points.

In temperate climates candles are usually made from mixed "stearine" and mineral waxes. Hence the unsaponifiable matter must be determined and examined.

(*b*) Mixed "Stearine" and Mineral Wax Candles

(α) PARAFFIN WAX

Since a description of the manufacture of *paraffin wax* falls outside the scope of this work, a few notes only can be given.[3] Paraffin wax is obtained from three sources, viz. crude petroleum, shale, and lignite.

In the crude petroleums the paraffin wax is contained ready formed as such ("protoparaffin"). In the shale and lignite the paraffin wax is formed by a process of destructive distillation ("pyroparaffin"). The raw material in shale appears to be exclusively of animal origin, and the formation of the hydrocarbons obtainable by destructive distillation would seem to take place by a process analogous to that occurring in the distillation of fish and liver oils, etc. (cp. Vol. I. Chap. I.). The raw material in lignite appears to be a bitumen having the chemical constitution of a monoatomic ester (" wax ") which can be extracted from the lignite by volatile solvents (see " Montan Wax," p. 291).

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[1] *Seifensieder Zeit.*, 1907, 1107.

[2] It may be added here that Kuess patents (French patent 367,448) a candle material containing, besides "stearine," paraffin wax, and neutral fats, the following ingredients: water, caustic potash, alum, and magnesium sulphate. Agostini (English patent 965, 1907; French patent 383,851) patents the incorporation of lead salts mixed with a fatty (drying) oil to candle material, especially to "paraffin" candles. Cp. also E. Burke, English patent 14,975, 1914.

[3] Cp. A. Campbell and W. Wilson, *Inst. Petrol. Techn.*, Jan. 21, 1919.

Petroleum Paraffin Wax.—Formerly North American petroleum (especially Pennsylvania crude) formed the chief source of this kind of paraffin wax. The proportion of paraffin wax in *American petroleum* varies from 2 to 4 per cent, but owing to the enormous amounts of petroleum raised in the United States very considerable quantities of paraffin wax were obtained from these fields. This is evidenced by the following table :—

Production of Paraffin Wax in the United States

	Barrels, of Average Weight, 378·3 lbs.	Value in Dollars.
1880	20,856	631,944
1890	241,951	2,904,902
1900	774,924	7,791,149
1905	794,068	10,007,274

Exports of Paraffin Wax from the United States

Year.	Lbs.	Dollars.
1900	182,153,718	8,602,723
1901	129,184,962	6,857,288
1902	173,583,203	8,858,844
1903	201,325,210	9,411,294
1904	188,651,119	8,859,964
1905	161,894,918	7,789,160
1906	178,385,368	8,808,245
1907	185,511,773	9,030,992
1908	178,709,678	8,740,929
1909	137,403,569	6,445,917
1910	196,982,550	7,886,359
1911	218,592,330	7,378,736
1912	249,502,699	8,123,486
1913	290,678,861	9,679,273
1914	186,357,728	6,516,338
1915	330,374,056	10,589,843
1916	360,650,114	12,873,250
1917	348,743,903	16,038,811
1918	235,543,481	22,273,612
1919	263,344,622	24,816,800
1920	375,276,359	32,619,318
1921	225,881,359	11,166,393

1918 and onward are calendar years; previous to that the statistics refer to fiscal years.

The countries to which the great bulk (including paraffin) is exported are shown in the following table :—

Exports to	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.	1912.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Great Britain	100,133,662	97,965,883	106,172,398[1]	99,728,401[1]	100,240,871[1]	80,986,209	101,667,475	95,880,046	116,870,807
Belgium	3,052,418	1,042,673	680,553	883,176	1,044,527	930,389	6,102,086	10,474,809	7,673,565
France	653,268	720,009	690,738	1,123,297	527,628	344,692	1,107,243	1,198,795	983,245
Germany	15,102,111	9,358,159	11,939,596	11,898,234	7,547,896	4,304,799	9,960,134	8,311,187	12,594,507
Italy	11,222,208	10,994,299	14,674,143	20,123,919	12,168,353	7,307,434	15,678,588	19,128,677	23,945,237
Holland	7,807,012	8,201,386	8,394,719	6,897,593	4,907,638	3,961,671	6,254,337	7,257,464	9,746,322
Mexico	8,778,801	7,431,469	8,731,025	11,755,550	11,527,878	14,334,311	9,920,264	12,629,149	16,388,014
Japan	13,618,753	9,754,347	11,291,260	6,928,986	16,045,602	5,355,166	8,867,284	15,724,510	14,573,132
British Australasia	1,935,851	2,833,917	4,094,302[2]	4,336,822	1,008,931	1,870,466	4,034,776	2,423,289	2,412,746
Asia	3,025,424	9,211,205	12,613,741	10,341,230	20,448,654	11,337,109	18,910,236	29,761,767	29,269,134
British Africa	2,089,545	2,144,062	1,652,931	3,265,941	3,116,826	1,671,335	5,161,136	6,991,313	4,957,600
Other countries	7,162,920	1,178,473	159,657,409	8,228,624	124,874	4,879,968	9,318,991	8,811,324	10,088,390
Total exports	174,581,973	160,835,882	178,385,368	185,511,773	178,709,678	137,403,569	196,982,550	218,592,330	249,502,699
Value in dollars	8,272,856	7,872,771	8,808,245	9,030,992	8,740,929	6,445,917	7,886,359	7,378,736	8,123,486

[1] Including Ireland.

[2] Including New Zealand.

Exports to	1913.	1914.	1915.	1916.	1917.	1918.	1919.	1920.	1921.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Great Britain	124,993,626	76,258,452	158,788,322	141,090,920	155,407,064	126,159,102	124,888,135	165,258,284	67,418,492
Belgium	6,762,322	3,690,197	894,543	...	...	...	7,616,088	1,830,518	4,555,092
France	1,454,905	573,137	12,753,313	17,876,917	20,167,674	10,096,902	16,748,872	4,302,765	672,976
Germany	19,023,883	3,806,460	725,089	...	...	...	...	9,249,150	9,539,179
Italy	25,280,185	16,715,352	64,394,562	55,450,573	48,765,695	28,023,343	16,765,920	48,819,380	93,556,073
Holland	12,967,181	6,337,142	5,639,977	3,013,728	888,594	...	...	6,979,464	2,599,645
Mexico	23,010,250	11,782,229	7,049,379	5,680,519	2,847,762	4,569,221	7,602,751	9,255,204	16,917,010
Japan	10,901,693	6,637,697	6,165,010	14,614,786	14,040,929	13,208,919	6,554,668	9,600,187	10,218,356
British Australasia	2,830,127	2,085,178	2,455,573	5,668,704	2,582,800	1,197,030	...[1]	...[1]	...[1]
Asia	34,438,358	20,485,920	26,419,475	38,086,552	34,856,493	21,652,384	...[1]	...[1]	...[1]
British Africa	8,776,783	16,198,665	8,303,854	16,326,718	14,917,998	1,568,410	...[1]	...[1]	...[1]
Other countries	20,239,548	21,787,299	36,784,959	63,840,727	54,268,894	29,068,170	83,168,188	119,981,407	20,404,536
Total exports	290,678,861	186,357,728	330,374,056	360,650,114	348,743,903	235,543,481	263,344,622	375,276,359	225,881,359
Value in dollars	9,679,273	6,516,338	10,589,843	12,873,250	16,038,811	22,273,612	24,816,800	32,619,318	11,166,393

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[1] Included in other countries.

At present the output of North American paraffin wax is falling off.

Most of the *Russian petroleums* contain only inconsiderable quantities of paraffin wax. The *Baku* petroleum yields practically none, the *Bibi-Eybat oil* small quantities only. The petroleum from the *Tcheleken Island* forms, however, an exception; this oil yields about 5·5 per cent of wax, which has appeared in the world's markets during the last few years. According to *Charitschkoff*[1] the petroleum from the western portion of the Grossny oil-fields yields 2·35 per cent of paraffin wax. Some crude petroleums in the *Ferghana districts* also contain sufficient paraffin wax to render its recovery a remunerative operation.

The *Roumanian* and *Galician petroleums* (with the exception of the *Boryslaw* and *Tustanowice petroleums*) yield less paraffin wax than do American petroleums. Petroleums from other sources do not, at any rate up till now, contribute to the production of paraffin wax. *Boryslaw* petroleum yields 5·6 per cent of paraffin wax.[2]

The largest amounts are at present obtained from *Rangoon petroleum*, which yields from 10 to 15 per cent of paraffin wax, melting at 138° F. *Assam wax* is obtained from a similar crude petroleum. This wax is brought into the market in two qualities, viz. "yellow wax" and "white wax." The latter melts at 140° F. These two paraffin waxes have the highest melting points of all commercial paraffin waxes. (It may be added that also from the American paraffin wax a product could be obtained of equally high, and even higher, melting point if the cost were not prohibitive. The author examined a sample of specially-prepared American paraffin wax, which had a melting point of 143° F.)

Paraffin wax from *Sumatra* crude oil has also appeared in the market during the last few years. At first this wax proved somewhat unsuitable for candle-making purposes, inasmuch as it was brittle and powdery; this difficulty has, however, been overcome by suitable treatment.

Lignite Paraffin Wax.—The Saxo-Thuringian lignite (brown-coal) tar industry[3] yields considerable quantities of paraffin wax. From this tar 10-15 per cent of wax is recovered by distillation. [Other methods of obtaining the paraffin wax from the lignite tar have been patented by *Pauli*[4] and by *Schultze*.[5]] The principal lignite-producing countries are Germany, the United States of America, Austria, and Hungary.

The output of finished candles in the Saxo-Thuringian candle industry amounts at present to about 8000 tons per annum, of which, however, a portion consists of "stearine" (see p. 299).

Shale Paraffin Wax.—The Scottish shale industry forms at present one of the most important sources of paraffin wax. The wax is obtained by refrigerating the higher boiling fractions of the shale oil, and purifying the paraffin scale by the "sweating process."[6] The yield of wax varies with the quality of shale; from best crude shale-tars as much as 15 per cent are obtainable.

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[1] *Chem. Revue*, 1909, 247.

[2] Zaloziecki, *Chem. Zeit.*, 1910, 265.

[3] Cp. Scheithauer, *Die Fabrikation der Mineralöle*, Braunschweig, 1895; E. Graefe, *Die Braunkohlenindustrie*, Halle a/S., 1906.

[4] Cp. *Jahrbuch d. Chem.*, 1901, xi. 370; 1902, xii. 376. German patent 123,101.

[5] German patent 162,341.

[6] Pyzel, English patent 22,313, 1910.

The importance of the Scottish shale industry is best exemplified by the fact that in the year 1904, 2,332,000 tons of shale were mined, which yielded 22,500 tons of paraffin wax (in addition to 6,293,200 gallons of naphtha, 17,000,000 gallons of burning oil, 38,000 tons of gas oil, 39,500 tons of lubricating oil, and 49,600 tons of ammonium sulphate [1]); whereas in 1909, 3,000,000 tons of shale were mined, from which there were produced 25,000 tons of paraffin wax, 20,000,000 gallons of burning oils, 3,000,000 gallons of naphtha, 22,000,000 gallons of lubricating and gas-making oils, and 54,000 tons of ammonium sulphate. Of less importance than the Scotch shale are the occurrences of shale in Wurtemberg,[2] at Messel in Hesse-Darmstadt, in Sweden,[3] France (Autun), and Brazil.[4] The Canadian shales (of which about 270,000,000 tons have been prospected in the Albert and Westmoreland counties of New Brunswick) may be worked up in the near future, as also the Torbanite of New South Wales.[5]

The chemical composition of paraffin wax is not yet fully known, and varies with its origin. The American paraffin wax may be considered as consisting principally of a mixture of hydrocarbons of the ethane series C_nH_{2n+2}. The paraffin wax produced in the Saxo-Thuringian lignite industry consists principally of saturated hydrocarbons, as will be seen from the following table, which enumerates the hydrocarbons isolated by *Krafft* [6] from a Saxo-Thuringian wax, which softened at the ordinary temperature:—

Formula.	Boiling Point at 0 mm. Pressure.	Melting Point. ° C.	Specific Gravity when Fluid.
$C_{19}H_{40}$ . .	109	31·8-32	...
$C_{20}H_{42}$ . .	117·5	36·3-36·6	0·7775
$C_{21}H_{44}$ . .	125·5	39·9-40·2	0·7778
$C_{22}H_{46}$ . .	130·5	44·0-44·5	0·7776
$C_{23}H_{48}$ . .	138	47·2-47·5	0·7799
$C_{24}H_{50}$ . .	145·5	50·7-51·3	0·7781
$C_{25}H_{52}$ . .	152·5	53·8-54	0·7785
$C_{26}H_{54}$ . .	160	56·8-57	0·7787
$C_{27}H_{56}$ . .	167	About 59·4	0·7789
$C_{28}H_{58}$ . .	173·5	About 61·6	0·7792
$C_{29}H_{60}$ . .	179	63·6-64·1	0·7797
$C_{30}H_{62}$ . .	186	65·6	0·7797
$C_{31}H_{64}$ . .	193·5	68·4	0·7799
$C_{32}H_{66}$ . .	201	69·8	0·7798
$C_{33}H_{68}$ . .	208	71·8	0·7801
$C_{34}H_{70}$ . .	215	About 73	0·7806
$C_{35}H_{72}$ . .	222	About 74	0·7813
$C_{36}H_{74}$ . .	About 230	About 76	0·7819

The author [7] found in a number of commercial paraffin waxes;

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[1] *Jahrbuch d. Chem.*, 1907, xvii. 414.

[2] *Ibid.*, 1904, xiv. 447.

[3] *Ibid.*, 1898, viii. 412.

[4] *Ibid.*, 1910, x. 397.

[5] *Ibid.*, 1905, xv. 431.

[6] *Berichte*, 1907, 4779.

[7] Unpublished observations.

melting from 132·5° to 138° F., percentages of carbon and hydrogen varying respectively from 85 to 85·59 per cent, and from 14·80 to 14·96 per cent. For a hydrocarbon of the saturated series theory requires for carbon 85·62 and for hydrogen 14·38 per cent.

Petroleum paraffin wax must not be considered as identical with the wax obtained by destructive distillation. As a rule, the paraffin wax obtained by destructive distillation is, in its technical applications, superior to petroleum paraffin wax.

In the trade crude paraffin wax is termed "scale." This contains varying quantities of impurities or "dirt," water, and hydrocarbons of lower melting point, consisting chiefly of "soft paraffin." The latter, being valueless to the candle-maker, is termed "oil."

There is no sharp line of demarcation between the solid hydrocarbons and "oil," as the hard paraffins pass gradually through "soft" or low melting point paraffins into "oil." The amount of "oil" pressed out in practical working naturally depends on various circumstances, such as temperature, pressure, length of time during which pressure is applied, etc. It will therefore be readily understood that a laboratory test for "oil" must be an arbitrary one.

Hence methods of testing are arranged by contract between buyer and seller and are laid down in specifications.

The methods agreed upon by the *Scottish Mineral Oil Association* and certain *Representative Purchasers* for the sampling and testing of scale are as follows[1] :—

Sampling of Scale.—The sample is taken by means of a metal tube, slightly conical, so that a cylindrical core of paraffin wax is obtained. Immediately after the sample has been drawn, it is thoroughly mixed and placed in suitable wide-mouthed bottles, which may be closed either with glass stoppers or good corks ; if the latter are used, they should be covered with paraffin paper or soaked in melted paraffin wax before being inserted. The scale should be tightly packed and should fill the bottles completely, as otherwise partial evaporation may occur, when moisture will condense on the upper portion. The bottles are then finally sealed in the usual manner.

Determination of Dirt in Scale.—The amount of dirt (fibres of press-cloths, sand, etc.) in scale is determined by melting a weighed quantity—not less than 7000 grains (453·58 grms.)—allowing to subside, and pouring off the clear paraffin wax. The residue is then mixed with naphtha or petroleum ether, thrown on a weighed dry filter paper, washed with the solvent used, dried, and weighed.

Determination of Water in Scale.—The amount of water present in scale may be determined by either of the following processes (the determination by "subsidence"[2] having been abandoned as leading to erroneous results) :—

(*a*) *Distillation from a Copper Flask.*—From 1 to 2 lbs. of the scale are heated in a copper flask connected with an ordinary Liebig condenser. The flask should be about 11″ high, 8″ in diameter at the bottom, and 1¼″ at the mouth. By means of a powerful Bunsen burner the water is volatilised and then condensed, a small quantity of light oil passing over at the same time. The distillate is received in a narrow graduated measure, so that the volume of water can be read off. As a little water usually adheres to the sides of the condenser tube, this must be washed off with petroleum ether or naphtha (previously saturated with water) and added to the bulk of the water.

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[1] *Journ. Soc. Chem. Ind.*, 1891, 346.

[2] Sutherland, *Journ. Soc. Chem. Ind.*, 1887, 123.

(*b*) *Price's Company's Method.*—500 grains (32·4 grms.) of the scale to be tested are weighed in a porcelain basin, and heated with constant stirring to 230° F. (110° C.), until bubbles cease to be given off; the loss is determined by weighing the residue.

500 grains (32·4 grms.) of the same scale, freed from water and dirt by melting at a gentle heat and by subsidence, are heated under exactly the same conditions (temperature, length of time) and the loss is determined. The loss now found is deducted from the loss ascertained previously; the difference is taken as the quantity of water present.

Determination of Oil in Scale.—A quantity of the scale, freed from water and dirt by melting and subsidence, is allowed to cool over night to a temperature of 60° F. (15·5° C.). The solid mass is then ground to powder, and a portion of this is used for the determination of oil.

250 grains (16·2 grms.) of the scale (or 150 grains = 9·6 grms. in the case of a scale containing much oil, *i.e.* over 7 per cent) are wrapped in fine linen press-cloth and a number of layers of filter paper, sufficient to absorb all the oil. The oil is then expressed in a press,[1] which must be provided with a pressure gauge.

The cup in which the scale is placed during the application of pressure must have an area of 20 square inches; the maximum pressure allowed is 10 cwts. per square inch, the working pressure being 9 cwts. per square inch. The scale must remain under pressure for fifteen minutes; the temperature of the scale and of the press should be 60° F.

Since the oil is determined in scale which has been freed from water and dirt, the result so obtained must be calculated to the original scale.[2] In Germany the "oil" was determined in a direct manner by *Holde's* method.

Holde operates as follows:—0·5 grm. of the wax is dissolved in 30 c.c. of ether, and 30 c.c. of 96 per cent alcohol are added. The mixture, after stirring, is cooled to 20° C., and the precipitate filtered off and washed with 10 c.c. of the alcohol-ether mixture. The insoluble wax is washed into a tared beaker with hot benzene, and after the evaporation of the solvent it is dried at 105° C. and weighed. The filtrate is evaporated to dryness and washed with 6 c.c. of the alcohol-ether mixture at a temperature of −20° C.; the weight of the insoluble portion is added to that of the first residue. The residue left on evaporation of the filtrate represents the amount of oil in the sample. The transparency of a sample of paraffin wax is no proof that it contains no oil, since *Singer* [1] found 3·6 per cent of oil in a transparent paraffin wax.

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[1] No special form of press is recommended for general adoption. A description of several forms of presses is given, *Journ. Soc. Chem. Ind.*, 1891, 346. Cp. also Carpenter and Leask, *Soap, Candles, etc.*, p. 324.

[2] For a direct method of determining oil in scale, based on the ready solubility of the "oil" in acetone, in which the hard paraffin wax is practically insoluble at 15° C., cp. L. Neustadl, *Chem. Zeit.*, 1906, 38. Jan Mijs Az (French patent 378,796) claims the purification of paraffin wax by means of acetone (methylalcohol, ethylalcohol, acetic acid, and acetic anhydride). Cp. also Graefe (*Chem. Zeit.*, 1907, 409).

Epstein and Polonyi [2] propose a method based on the depth of the colour developed when a wax containing oil is mixed with picric acid.

The finished material of the Scottish paraffin industry is sold as "soft" paraffin wax if its solidifying point be below 48° C. = 118° F. Paraffin wax of a melting point above 120° F. is termed "hard" paraffin wax. The candle material produced in the Saxo-Thuringian industry has, as a rule, a melting point of 53°-56° C.; material of lower melting point (50°-52° C.) or higher melting point (60° C.) is but rarely produced. The melting points of Rangoon and Assam commercial paraffin waxes have been given above (p. 268).

Besides colour, transparency,[3] and odour, the most important criterion in the valuation of paraffin wax is the determination of the melting point. The specific gravity is of minor importance. Still, in controlling the process of manufacture, the following tables will be found useful:—

Specific Gravity of Paraffin Waxes (Allen) [4]

No.	Origin of Sample.	Specific Gravity.		Solidifying Point.
		Solid, at 15° C.	Liquid, at 99° C.	° C.
1	Shale oil . . .	0·8666	0·7481	44·0
2	,, . . .	0·8961	0·7494	47·0
3	,, . . .	0·9000	0·7517	52·0
4	,, . . .	0·9111	0·7572	58·5
5	American petroleum .	0·9083	0·7535	53·8
6	Rangoon tar . .	0·8831	0·7571	49·0

Specific Gravities of Refined American Paraffin Waxes (I. Redwood) [5]

°F. at which the Gravity was determined.	Melting Point 108° F.	Melting Point 114° F.	Melting Point 120·5° F.	Melting Point 122·25° F.	Melting Point 122·75° F.	Melting Point 128·25° F.	Melting Point 133·25° F.
160	0·77069	0·77193	0·77391	0·77079	0·77023	0·77573	0·77723
155	0·77119	0·77330	0·77531	0·77149	0·77163	0·77653	0·77853
150	0·77309	0·77473	0·77657	0·77319	0·77283	0·77803	0·78003
145	0·77509	0·77620	0·77777	0·77519	0·77463	0·77973	0·78153
140	0·77679	0·77763	0·77847	0·77689	0·77633	0·78133	0·78333
135	0·77899	0·77953	0·78147	0·77869	0·77843	0·78303	...
130	0·78049	0·78113	0·78267	0·78029	0·77973	...	...
125	0·78199	0·78343	0·78441	...	...	...	...
120	0·78359	0·78473	...	...	...	...	...
115	0·78529	...	...	...	...	...	...

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[1] *Journ. Soc. Chem. Ind.*, 1909, 789.

[2] *Petroleum*, 1912, 594.

[3] Transparency is not a proof that it is free from oil.

[4] *Comm. Org. Anal.* vol. ii. p. 411.

[5] *Journ. Soc. Chem. Ind.*, 1889, 163.

Specific Gravities of American Paraffin Waxes at 60° F. (I. Redwood)

Melting Point 106° F.	Melting Point 111·5° F.	Melting Point 120·5° F.	Melting Point 122·25° F.	Melting Point 125·75° F.	Melting Point 131° F.
0·87525	0·88230	0·89895	0·90105	0·90350	0·90865

The subjoined table, due to *Tervet*,[1] gives the melting points of each of twenty successive fractions into which three paraffin waxes of the given melting points have been resolved. The temperatures are degrees Fahrenheit.

Melting Points of Fractions obtained from Paraffin Waxes

No. of Fraction.	Of Melting Point 126° F.	Of Melting Point 111° F.	Of Melting Point 102° F.
1	119·0	103·0	94·0
2	120·0	104·0	94·0
3	120·5	104·5	95·0
4	121·0	105·0	96·0
5	121·0	106·0	96·0
6	121·0	107·0	97·5
7	121·5	107·5	98·0
8	122·0	108·0	98·5
9	122·5	108·5	99·0
10	123·0	109·0	99·0
11	124·0	110·5	100·0
12	125·0	112·0	102·0
13	126·0	113·0	103·5
14	127·0	113·5	105·0
15	128·0	114·5	106·5
16	129·0	116·0	108·0
17	130·0	117·0	109·0
18	132·0	119·0	110·0
19	134·0	123·0	112·5
20	138·0	125·0	113·0

A uniform method of determining the solidifying point (or setting point) of paraffin wax has not yet been universally agreed upon. Hence in commercial analysis three different methods are in vogue, known as the "English test," the "American test," and the "German test," respectively.

English Test.—A test-tube, about 1 inch in diameter, is filled to the depth of about 2 inches with the melted paraffin, a small thermometer is inserted, and the mass stirred steadily, while the test-tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for a short time is the melting (setting) point. It should be noted that paraffin wax does not behave like mixed fatty acids, which on solidifying exhibit a sudden rise of temperature (Vol. I. Chap. VIII.). With paraffin wax the mercury column of the thermometer remains stationary at the melting point for about half a minute; but no rise takes place, and the mercury then falls steadily.

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[1] *Journ. Soc. Chem. Ind.*, 1887, 356.

In order to render the indications more definite, the author takes larger quantities than directed above, using a test-tube of the same size as described for the titer test (Vol. I. Chap. VIII.). The stirring is interrupted when the solidification point is almost reached, and the fall of temperature is then observed from minute to minute; that point at which the mercury column remains stationary the longest time is taken as the solidifying point. The following example will best illustrate an observation:—

Time.	Temperature °F.	Time.	Temperature °F.
3·12	145	3·23	124·75
3·13	143	3·24-3·28	124·5
3·15	137·5	3·29-3·32	124·25
3·16	135	3·33-3·35	124·1
3·17	133	3·36-3·46	124
3·18	130·5	3·47	123·9
3·19	129·5	3·48	123·85
3·20	127	3·49	123·60
3·21	126	3·50	123·50
3·22	125	...	...

The thermometer remained stationary for fourteen minutes at about 124° F., and therefore this number is returned as the solidifying point. A similar suggestion has been made by *Fischer*,[1] who carries out the titer-test method in the manner proposed by *Finkener*, and described under "Titer test" (Vol. I. Chap. VIII.), using a 150-c.c. flask. The indications become thereby still more distinct, but as an experiment carried out by the author according to *Fischer's* directions required two and a half hours, as against about forty minutes for the smaller quantity, it will be found more useful to employ about 50 grms. of material.

American Method.—The melting point is determined as follows:—A sufficient quantity of wax is melted to fill three parts of a half-round dish, three and three-fourth inches in diameter. A thermometer with a round bulb is suspended in the melted mass so that the bulb is only three-fourths immersed. The melted paraffin is then allowed to cool slowly, and the temperature at which occurs the first indication of "filming," extending from the sides of the vessel to the thermometer, is taken as the melting point.[2]

German Method ("*Hallenser Vorschrift*").—A small beaker, 7 cm.

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[1] *Zeits. f. angew. Chem.*, 1906, 1323.

[2] Garrigues (*Journ. Soc. Chem. Ind.*, 1895, 281) proposes to take this point by melting 30 to 50 grms. of the sample in a beaker, inserting the thermometer so that the bulb is completely immersed, and twirling the beaker continuously in one direction until the mercury ceases either to fall or rise. At first it falls rapidly and regularly, then more steadily at the rate of 0·1° to 0·20° C. per minute until it reaches a point at which it remains stationary for about half a minute. This point is taken as the melting point.

high and 4 cm. in diameter, is filled with water and warmed to about 70° C. A small piece of the sample of paraffin wax is then thrown on to the water so as to form, after melting, a disc of about 6 mm. diameter. A centigrade thermometer,[1] made according to the directions of the *Halle Association*, is then immersed in the water so that the bulb is entirely covered, and the mass is allowed to cool slowly. The temperature at which a film is observed on the paraffin wax is noted as the solidifying point.[2] This method has been somewhat modified without, however, increasing its reliability.[3] The indications furnished by this test are criticised by *Graefe*.[4]

It is evident that the determination of the solidifying point, according to the American and German methods, must lead to very uncertain results. The best plan is to adopt the "English" method, with the author's modification described above. With reference to the German method, it may be stated that the manufacturers of lignite paraffin wax are likely to adopt *Shukoff's*[5] method (Vol. I. Chap. VIII.). In the commercial valuation of Galician paraffin wax, *Shukoff's* method is used almost exclusively.[6] *L. Weinstein*[7] has shown that the results obtained by the capillary tube method are very concordant.

In order to show that the melting and solidifying points of paraffin waxes do differ (cp. above, p. 237, cp. also below, "Ceresin"), a few numbers due to *Lewkowitsch* are appended[8]:—

Paraffin Wax.	Melting Point. Capillary Tube.	Solidifying Point.
Rangoon	136·5° F. = 58·05° C.	135·75° F. = 57·65° C.
Scotch	132° F. = 55·5° C.	128° F. = 53·5° C.

K. Friche determines the rate of solidification by observing the time required for a wax to set to such a consistence that a weighted iron rod will make no impression on it.[9]

Breth states[10] that different parts of block paraffin wax will show different solidification points, the wax from the centre of the block having the highest.

Candles made exclusively from the ordinary paraffin wax, melting point 120° F., are too soft and bend too easily for ordinary purposes. Hence, in the manufacture of paraffin candles, from 5 to 15 per cent of "stearine" is usually admixed with the paraffin wax.[11]

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[1] This thermometer is supplied by *Ferd. Dehne*, or *J. H. Schmidt*, Halle a/S.

[2] *Journ. Soc. Chem. Ind.*, 1887, 567; cp. also Kissling, *Chem. Zeit.*, 1898, 2; *Chem. Revue*, 1904, 217.

[3] Cp. Fischer, *Zeits. f. angew. Chem.*, 1906, 1323.

[4] *Laboratoriumsbuch f. d. Braunkohlenteer Ind.*, 1908, 74.

[5] With regard to a criticism of this method by Kissling, cp. *Chem. Revue*, 1909, 46, and Shukoff's reply (*Ibid.*, 1908, 112).

[6] Singer, *Petroleum*, 1909, 1038.

[7] *Chem. Zeit.*, 1887, 784.

[8] Cp. also Graefe, *Chem. Zeit.*, 1904, 1144.

[9] *Chem. Zeit.*, 1921, 45, 891.

[10] *Petroleum*, 1911, 106.

[11] Other paraffin candle hardeners ("candle stiffener"), ceresin and montan wax, are described below (p. 284); hydroxystearic acid has been mentioned already. The addition of acidyl derivatives of aromatic bases, such as stearic anilide, stearic-p-toluidide, stearic-β-naphthylamide, stearic-m-phenylenediamide, etc., has been patented by Liebreich (French

The melting points of a mixture of paraffin wax and stearine cannot be calculated from the melting points of the components (cp. Vol. I. Chap. III.). It is therefore necessary for the proper control of the manufacture that each works chemist construct an empirical table from the melting points of his special materials. Such empirical tables are given below for (*a*) mixtures of Scotch paraffin wax and "stearine," and (*b*) mixtures of Thuringian paraffin wax and "stearine."

(*a*) *Melting Points of Candle Material from "Mixed Paraffin Wax" (Scotch Pyroparaffin) and "Stearine" (I. Redwood)*

A

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	102	10	121	100
80	,,	20	,,	98·5
70	,,	30	,,	100
60	,,	40	,,	104·5
50	,,	50	,,	110·5
40	,,	60	,,	111·0
30	,,	70	,,	113·5
20	,,	80	,,	117·5
10	,,	90	,,	119·0

B

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	120	10	123	118
80	,,	20	,,	116·50
70	,,	30	,,	114
60	,,	40	,,	112
50	,,	50	,,	110
40	,,	60	,,	109
30	,,	70	,,	113
20	,,	80	,,	118·50
10	,,	90	,,	119·50

patent 322,026; German patent 136,917; cp. also German patent 136,274). The advantage (cp. also Lewkowitsch, *Jahrbuch d. Chem.*, 1902, xii. 370) of this admixture was supposed to consist in the candle material having a higher melting point than without this addition. Graefe (*Chem. Zeit.*, 1904, 1144) has, however, shown that the alleged raising of the melting point is a fictitious one, inasmuch as the anilides, which melt at a higher temperature, float in the melted paraffin, and require further heating before the substance in the capillary tube is completely melted (cp. also Spiegel, *Chem. Zeit.*, 1906, 1235; Graefe, *ibid.*, 1907, 19); O. Kulka, *Chem. Revue*, 1909, 30; Easterfield and Taylor patent the use of stearone produced by the interaction of stearic acid with iron filings at a high temperature.

C

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	120·25	10	129·75	118·50
80	"	20	"	116·75
70	"	30	"	114·50
60	"	40	"	112·25
50	"	50	"	113
40	"	60	"	118·75
30	"	70	"	122
20	"	80	"	124·50
10	"	90	"	127

D

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	125	10	121	123
80	"	20	"	121
70	"	30	"	119
60	"	40	"	117·50
50	"	50	"	114
40	"	60	"	111
30	"	70	"	107
20	"	80	"	114
10	"	90	"	117

E

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	130	10	121	128
80	"	20	"	125·50
70	"	30	"	123
60	"	40	"	121
50	"	50	"	118·50
40	"	60	"	114
30	"	70	"	109
20	"	80	"	115·50
10	"	90	"	118

F

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	132·50	10	129·75	130·50
80	,,	20	,,	128·50
70	,,	30	,,	126·50
60	,,	40	,,	124·25
50	,,	50	,,	121·0
40	,,	60	,,	117·75
30	,,	70	,,	119·50
20	,,	80	,,	125·25
10	,,	90	,,	127·50

(*b*) *Melting Points of Candle Material from "Mixed Paraffin Wax" (Thuringian Pyroparaffin) and "Stearine" (Scheithauer)*[1]

Paraffin Wax. Per cent.	Of Melting Point. °C.	"Stearine" of Melting Point 54° C. Per cent.	Melting Point of Mixture. °C.
90·0	36·5	10·0	36·5
66·6	,,	33·3	39·0
33·3	,,	66·6	45·75
10·0	,,	90·0	51·75
90·0	37·5	10·0	36·5
66·6	,,	33·3	35·5
33·3	,,	66·6	47·0
10·0	,,	90·0	52·0
90·0	40·75	10·0	39·75
66·6	,,	33·3	40·50
33·3	,,	66·6	47·50
10·0	,,	90·0	52·0
90·0	45·0	10·0	44·0
66·6	,,	33·3	40·75
33·3	,,	66·6	48·0
10·0	,,	90·0	52·5
90·0	48·5	10·0	47·5
66·6	,,	33·3	45·0
33·3	,,	66·6	47·75
10·0	,,	90·0	52·50
90·0	50·0	10·0	49·0
66·6	,,	33·3	47·0
33·3	,,	66·6	47·5
10·0	,,	90·0	52·5
90·0	54·0	10·0	53·0
66·6	,,	33·3	49·0
33·3	,,	66·6	47·0
10·0	,,	90·0	52·5
90·0	56·5	10·0	55·5
66·6	,,	33·3	52·0
33·3	,,	66·6	47·5
10·0	,,	90·0	52·5

In the Thuringian industry five kinds of paraffin candles are produced: (1) Candles of the melting point 53°-54° C. ("*Adlerkerzen*"); (2) Candles of the melting point 54°-55° C. ("*Brillant-*

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[1] *Die Fabrikation der Mineralöle*, Braunschweig, 1895.

kerzen"); (3) Candles of the melting point 55°-56° C. ("*Kronenkerzen*," "*Salonkerzen*"); (4) Candles of the melting point 56° C. ("*Baumkerzen*"); and (5) Candles made from 33·3 per cent stearine, and 66·7 per cent paraffin wax ("*Kompositionskerzen*"). (*Höland.*[1])

The differentiation of paraffin waxes obtained from different sources is a very difficult problem. It cannot be effected with the aid of the melting points, of the iodine values,[2] or of the refractive index.[3] *Graefe*[4] suggests as a method of differentiating "protoparaffins" from "pyroparaffins" to treat the sample with an equal volume of concentrated sulphuric acid of 66° Bé.; the "protoparaffins" are stated to remain light-coloured and impart to the sulphuric acid layer only a slight coloration, the acid itself remaining clear, whereas the "pyroparaffins" become brown or yellow, and the sulphuric acid layer is turbid.[5] A method may perhaps be based on the solubility in absolute alcohol.[6] The paraffin waxes from petroleum are comparatively easily soluble in absolute alcohol, whilst the Saxo-Thuringian waxes are much less soluble in this menstruum. (Ceresin in almost insoluble.)

Holde records the following solubilities for a petroleum paraffin wax :—[7]

100 parts of absolute alcohol dissolve at 20° C. 0·1-0·19 parts
100 „ „ „ „ 15° C. 0·015-0·017 „

whereas the Saxo-Thuringian paraffin waxes of melting point 55-56° C.[8] gave the following data :—

100 cc. of 99·5 per cent alcohol dissolve 0·031 grms. at 0° C.
100 cc. of 98·5 „ „ „ 0·029 grms. at 0° C.

In the case of soft paraffin waxes (such as are obtained in the Saxo-Thuringian industry) the solubility in alcohol increases with the decrease of the melting point.[9] The lower the melting point the greater is the loss by volatilisation at temperatures ranging from 100° to 125° C. The following table given by *Eisenlohr* for soft Saxo-Thuringian paraffin waxes is instructive :—

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[1] *Zeits. f. angew. Chem.*, 1903, 614.

[2] Cp. Lewkowitsch, *Jahrbuch d. Chem.*, 1905, xv. 430.

[3] Marcusson and Meyerheim, *Zeits. f. angew. Chem.*, 1901, 1059.

[4] *Zeits. f. angew. Chem.*, 1905, 1580.

[5] Cp. also Istrati and Michailescou, *Chem. Zentralbl.*, 1904, ii. 1447.

[6] Höland, *Zeits. f. angew. Chem.*, 1903, 614.

[7] *Chem. Revue*, 1898, 114.

[8] Although the origin was not stated, the wax was most likely a Saxo-Thuringian wax, since the numbers given above have been confirmed by Eisenlohr, *Zeits. f. angew. Chem.*, 1897, 334, for a lignite paraffin wax of the melting point 55·5° C.

[9] Eisenlohr, *Journ. Soc. Chem. Ind.*, 1897, 701.

Paraffin Wax of Melting Point.	Loss by Volatilisation.	
	At 100° C.	At 125° C.
° C.	Per cent.	Per cent.
29·5	10·0	...
33·0	...	18·5
38·0	1·4	...
48·0	...	1·8

Graefe[1] ascertained the following solubilities for a Thuringian paraffin wax melting at 53·5° C. :—

1 c.c. of	dissolves at 20° C.
Ethyl acetate	1·1 milligrams
Acetone	1·2 ,,
Alcohol (96 per cent) . . .	1·9 ,,
Ether	83·4 ,,
Petroleum ether	200 ,,
Ligroïn	244 ,,
Chloroform	246 ,,
Benzene	285 ,,
Carbon tetrachloride . . .	317 ,,

(β) CERESIN (OZOKERITE PARAFFIN)

The raw material used for the production of ceresin is *ozokerite*, a natural bituminous product occurring in many parts of the globe in the vicinity of petroleum springs. The best known ozokerite is the Galician.[2] The ozokerite (" Neftgil ") occurring on Tcheleken Island (the petroleum found there contains 5·5 per cent of paraffin wax, p. 268) is much softer and darker than the Galician. Ozokerite is also found in Roumania,[3] in Utah,[4] in the Argentine, and in the Orange Free State.

The export of ozokerite for the first half of 1909 from Austro-Hungary is stated to have been 1117 tons, £67,500.

It is reported that rich pockets of ozokerite have been found in Hungary (district Körösmezo) at a depth of 270 feet. It is further stated that, above this ozokerite layer, petroleum has been found at a depth of 60 to 80 feet.

It is noteworthy that the hardness of the ozokerite decreases as the layer increases in depth. Thus the " marble wax " (" Boryslawite ") is found frequently to a depth of 300 feet; at a depth of 600 feet it disappears altogether. At this latter depth a salve-like wax (" kendebal "), which is a mixture of paraffin wax and petroleum, is found.

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[1] *Chem. Revue*, 1906, 30.

[2] Cp. J. Berlinerblau, *Das Erdwachs, Ozokerit und Ceresin*, 1897; J. Muck, *Der Erdwachsbergbau in Boryslaw*, 1903.

[3] Istrati and Michailescou, *Chem. Zentralbl.*, 1904, ii. 1447.

[4] Cp. E. B. Gosling, *School of Mines Quarterly*, 16 [1], 41.

It would thus appear that in the case of the "kendebal" the lighter component of the original petroleum has not yet evaporated off, or has not yet risen to a higher level.

As regards the origin of ozokerite, the opinion expressed by some writers that it is an intermediate product between glycerides and petroleum (see Vol. I. Chap. I.) does not seem to be so well supported by facts as is the theory which regards ozokerite as a natural petroleum residue, for ozokerite-like masses can be obtained from many petroleums by separating from the oil a residue which either settles on standing or can be obtained after the more volatile hydrocarbons have been removed by gentle heating. These separated masses themselves are not paraffin wax, but form paraffin wax on heating.

The upper layers carrying the best ozokerite are gradually becoming exhausted, and the boring extends to lower depths than has been the case some time ago. Thus the upper stratas of Boryslaw are exhausted and workings now extend to a depth of about 1000 ft. A curious observation which has been made is that with the increasing depth of the layers the raw material approaches more and more the character of a paraffin wax. This throws some light on the theory of the formation of ozokerite, and would point to the fact that the above-given explanation that ozokerite is the final product of the change undergone on exposure to the atmosphere, is the correct one.

The colour of crude ozokerite varies from pure yellow to dark brown, the shade depending on the amount of admixed oxygenated resinous products.

The specific gravity of the crude ozokerite varies from 0·91 to 0·97. The melting point depends on the proportion of liquid hydrocarbons contained in the ozokerite. It is therefore difficult to fix a lower limit for the melting point; the upper limit of about 100° C. is reached by the so-called "marble-wax" ("Boryslawite"). In the lower qualities the melting point falls to about 50° C.

The crude ozokerite as mined is freed from water and mineral matter, clay, etc., by a liquating process, and by boiling out with water. The thus purified ozokerite consists chiefly of hydrocarbons, but contains also oxygenated and wax-like bodies. The degree of facility with which crude ozokerite can be kneaded between the fingers affords a rough test for valuing. The longer ozokerite has been kept at a temperature above 70° C., and the more carefully the liquation process has been conducted, the purer will be the ceresin obtained from it (see below). Fraudulently added impurities are: asphaltum (mineral pitch), and residues from paraffin oil distilleries.

In the examination of ozokerite the loss on heating to 150° C. (which should not exceed 5 per cent), the melting and solidifying points, and the proportion of mineral matter should be determined. To estimate the mineral substances, small pieces are cut from the bottom of the blocks of ozokerite and exhausted with petroleum ether.

Ozokerite can only be properly valued by closely following the process of refining adopted on the large scale.

Ozokerite was formerly distilled in a current of superheated steam with a view to converting it into white "paraffin wax." The yield from a good crude material varied from 60 to 70 per cent.

A "paraffin wax" thus obtained has been studied by *Pawlewski and Filemonewicz* with regard to its behaviour with solvents.[1] The ozokerite paraffin had the specific gravity of 0·9170 at 20° C., melted at 64°-65° C., and solidified at 61°-63° C.

Solvent.	Grms. of Ozokerite Wax dissolved by		Weight of Solvent required to dissolve completely 1 Part of Ozokerite Wax.
	100 grms.	100 c.c.	
Carbon bisulphide	12·99	...	7·6
Petroleum ether, boiling up to 75° C.; spec. grav. = 0·7233	11·73	8·48	8·5
Oil of turpentine, boiling point 158°-166° C.	6·06	5·21	16·1
Cumene, comm., boiling up to 160° C.; spec. grav. = 0·867	4·28	3·72	23·4
Cumene fraction, 150°-160° C.; spec. grav. = 0·847	3·99	3·39	25·0
Xylene, comm., boiling point 135°-143° C.; spec. grav. = 0·866	3·95	3·43	25·1
Xylene, boiling point 136°-138° C.; spec. grav. = 0·864	4·39	3·77	22·7
Toluene, comm., 108°-110° C.; spec. grav. = 0·866	3·83	3·34	26·1
Toluene, boiling point 108·5°-109·5° C.; spec. grav. = 0·866	3·92	3·41	25·5
Chloroform	2·42	3·61	41·3
Benzene	1·99	1·75	50·3
Ethyl ether	1·95	...	50·8
Isobutyl alcohol, spec. grav. = 0·804	0·285	0·228	352·9
Acetone, 55·5°-56·5° C.; spec. grav. = 0·797	0·262	0·209	378·7
Ethyl acetate	0·238	...	419·0
Ethyl alcohol, 99·5° Tr.	0·219	...	453·6
Amyl alcohol, 127°-129° C.; spec. grav. = 0·813	0·202	0·164	495·3
Propionic acid	0·165	...	595·3
Propyl alcohol	0·141	...	709·4
Methyl alcohol, 65·5°-66·5° C.; spec. grav. = 0·798	0·071	0·056	1447·5
Methyl formate	0·060	...	1648·7
Glacial acetic acid	0·060	0·063	1668·6
Ethyl alcohol, 64·3° Tr.	0·046	...	2149·5
Acetic anhydride	0·025	...	3856·2
Formic acid (cryst.)	0·013	0·015	7689·2
Ethyl alcohol, 75° Tr.	0·0003	...	330000·0

The comparative solubilities of paraffin wax of the melting point 53·7° C. and ceresin of the melting point 68·7° C. are given by *Chercheffsky*[2] as follows:—

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[1] *Journ. Chem. Soc.*, 1889; Abstr. 82.

[2] *Les Matières grasses*, 1911, 2236.

Solvent.	Amount dissolved in 100 c.c. at 15° C.	
	Ceresin.	Paraffin.
Ethyl alcohol, 96·5 per cent	0·056	0·108
Methyl alcohol, 99·25 per cent	0·016	0·004
Amyl alcohol, b.p. 129°-131° C.	0·100	0·496
Carbon bisulphide	1·9716	19·072
Carbon tetrachloride	1·948	11·784
Chloroform	1·276	5·332
Benzene	0·784	4·540
Acetone, 54/58° C.	0·028	0·120
Ethyl ether	0·592	1·920

At present ozokerite is exclusively worked up for the preparation of ceresin. It would, of course, be extremely wasteful to distil ozokerite destructively (as has been done experimentally), valuable material thereby being converted into gas, coke, and comparatively valueless hydrocarbons, boiling from 100° C. upwards. For the commercial valuation of ozokerite, *Lach*[1] recommends the following process :—

100 grms. of ozokerite are treated in a tared porcelain basin with 20 grms. of fuming sulphuric acid at a temperature of 170°-180° C. with constant stirring, until sulphur dioxide is no longer given off. After cooling, the dish is weighed and the loss taken as the sum of water and hydrocarbons. The mass is then again melted and 10 grms. of animal char, previously dried at 140° C., are stirred in. A tenth part of this mixture is weighed off in a paper thimble, and extracted in a *Soxhlet* apparatus with petroleum ether boiling below 80° C. The filter is dried at 130° C. and weighed ; the difference gives the ceresin. The result may be checked by evaporating the petroleum ether solution and drying the residue at 180° C. The melting point of the isolated ceresin is then ascertained. The proportion of fuming sulphuric acid may be varied, according as the colour of the refined product is desired to be yellow or white. *E. von Boyen*[2] states that even 5 grms. of ozokerite are sufficient for a satisfactory technical analysis.

The refined product, termed **Ceresin** (French, *Céresine* ; German, *Ceresin, Erdwachs*) on account of its resemblance to beeswax (and also because of its property of occurring only in an amorphous form), is obtained on a large scale in the same manner as in the above technical analysis. The crude ozokerite is heated with sulphuric acid whilst being stirred constantly. The conditions, namely, quantity of acid, temperature, and time of interaction, must be carefully observed and adapted to the raw material, as excess of acid, too high a temperature, and too prolonged time of interaction lead not only to great loss but also to an inferior product, in that the elastic properties of ceresin are injured to a large extent. The resulting material is decolorised with char and filtered through a filter press. The cakes left in the filter press are extracted with volatile solvents to recover the retained ceresin.[1] The ceresin is, as a rule, yellow, but can be made white and odourless by further refining processes. It melts between 61° and 78° C.; the so-called "Sprungwachs" melts at 75°-80° C.; its specific gravity varies from 0·918 to 0·922.

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[1] *Journ. Soc. Chem. Ind.*, 1885, 488.
[2] *Zeits. f. angew. Chem.*, 1898, 383.

Tilden[2] obtained a crystalline hydrocarbon from ozokerite by heating it with concentrated sulphuric acid for some hours, washing, distilling, and crystallising the solid distillate from alcohol. The hydrocarbon approximated the composition $C_{28}H_{58}$ and melted at about 65° C.

Rakusin[3] stated that ceresin is optically active, whereas *Engler*[4] found several samples of (ozokerite and) ceresin to be optically inactive.

The most important test in the valuation of ceresin is the determination of its melting point. The various methods used in commercial analysis give different results, as may be exemplified by a sample of ceresin examined in my laboratory. The melting point by *Pohl's* method (Vol. I. Chap. IV.) (which was stipulated in the contract) was 151° to 157° F. By the capillary tube method the point of incipient fusion was found to be 146° F., and the point of complete fusion 154° F. By the "English method" (p. 273) the melting point was 148° to 150° F. This shows the necessity of laying down in contracts the method by which the sample should be tested.

The method proposed by *Finkener*[5] for Custom House purposes, viz. to determine the dropping point of ceresin, with a view to distinguishing ceresin from mixtures of ceresin and paraffin wax, has been criticised by *Holde*,[6] who showed that mixtures can be prepared from ceresin and paraffin wax, having dropping points considerably higher than 66° C. (the lowest limit laid down by *Finkener* for pure ceresin); moreover, mixtures of pure ceresin and carnaüba wax may "drop" at a point which lies far above that temperature, and the presence of paraffin wax in the mixture can be easily masked by adding carnaüba wax. This method cannot, therefore, be recommended.

Ceresin, owing to its high price, is very extensively adulterated with paraffin wax and bleached rosin. In order to raise the melting point of such a mixture carnaüba wax is frequently added. Rosin is detected by a definite acid value of the sample and by the *Liebermann-Storch* reaction.[7] Carnaüba wax is detected in the unsaponifiable matter by the method described in Vol. I. Chap. IX.

Commercial ceresin is frequently coloured with turmeric, as also with tar colours. On shaking the melted sample with alcohol the colouring matters pass into the alcoholic solution, which may then be further examined (cp. Vol. II. p. 808, under "Butter").

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[1] Cp. *Zeits. f. angew. Chem.*, 1899, 1172.
[2] *Journ. Chem. Soc.*, 1905, 562.
[3] *Chem. Zeit.*, 1905, 156.
[4] *Ibid.*, 1906, 711.
[5] *Mitth. Königl. Techn. Versuchsanstalten*, 1899, vii. 100.
[6] *Ibid.*, p. 103. Cp. Bindewald, *Chem. Zeit.*, 1903, 433.
[7] Under the name "Aëresin" oxidised rosin oil is sold as an adulterant of ceresin.

Since *paraffin wax* is much more readily soluble in absolute alcohol than is ceresin (which is almost insoluble in this menstruum), paraffin wax may be detected in ceresin by heating the sample with absolute alcohol, allowing to cool, and placing a few drops of the alcoholic solution on an object-glass, when the residue will appear crystalline under the microscope. This method yields very uncertain results.

Armani and Rodano [1] determine the turbidity temperature of mixtures of ceresin and paraffin wax by dissolving 0·1 grm. in 10 c.c. of a mixture of equal parts of absolute alcohol and benzene. The solution is allowed to cool slowly and the temperature at which a turbidity appears is noted. The following turbidity temperatures have been determined :—

Ceresin. Per cent.	Paraffin Wax. Per cent.	Turbidity Temperature. ° C.
100	0	50
90	10	48
80	20	47·5
70	30	47
60	40	44·5
50	50	43
40	60	41·5
30	70	40
25	75	38
20	80	36·5
10	90	30
5	95	27
0	100	20-28

The following table, due to *Berlinerblau*, may furnish some additional means of ascertaining the purity of a given sample :—

Ceresin. Per cent.	Paraffin Wax. Per cent.	Melting Point. ° C.	Solidifying Point ° C.	Specific Gravity at		
				15° C.	83°-85° C.	95° C.
100	0	70-73	69·5	0·921	0·7835	0·774
95	5	69-73	68·5	0·919		
90	10	68-72	66·5	0·9175	0·7800	
80	20	66-71·5	65·0	0·914	0·7775	
70	30	64·5-70	63·0	0·910	0·7750	
60	40	62-69	62·0	0·907		
50	50	58·5-67	60·0	0·904	0·7705	
40	60	56·5-65	59·0	0·900		
30	70	54·5-62	57·0	0·897		
20	80	52·5-58·5	54·0	0·894		
10	90	49·5-54·5	49·0	0·892		
0	100	47-52	47·0	0·889	0·7655	0·756

Graefe [2] has shown that admixtures of ceresin—from 1 per cent to

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[1] *Ann. Lab. Chim. Centr. delle Gabelle*, 1912, vi. 109.

[2] *Chem. Zeit.*, 1903, 248.

10 per cent—with paraffin wax cannot be detected by the determination of the solidifying point, since a paraffin wax of the solidifying point 54·8° C. when admixed with quantities of ceresin varying from 1 to 10 per cent still gave the same solidifying point, viz. 54·8° C.

The detection of small quantities of ceresin in paraffin wax is carried out by *Graefe* in the following manner :—

One grm. of the sample is dissolved at 20° C. in 10 c.c. of carbon bisulphide. In case more than 10 per cent of ceresin be present, no clear solution is obtained at 20° C. If the solution has remained clear, 1 c.c. is shaken in a test-tube with a mixture consisting of 5 c.c. of ether and 5 c.c. of 96 per cent alcohol, and kept at 20° C. In case the sample consists of pure paraffin wax (Saxo-Thuringian) of a melting point up to 54° C., no separation takes place ; if, however, ceresin be present, flocks separate, simulating somewhat the appearance of alumina precipitated by ammonia from a very dilute solution. *Graefe* states that even 1 per cent of ceresin can thus be detected.

In the case of paraffin wax of a higher melting point than 54° C., the method breaks down, as such wax gives a precipitate with the ether-alcohol mixture, though the appearance of this differs from that obtained with pure ceresin. *Sommer*[1] objects to this method on the ground that only American and Saxo-Thuringian paraffin waxes behave as described above, whilst Scotch, Galician, and the high melting "Java" paraffin waxes might be considered to represent a mixture of paraffin wax and ceresin, if judged solely by this test. Yet *Graefe*[2] maintains that his own method yields correct results, but observations made in the author's laboratory (by *Heymann*) on Scotch hard paraffin waxes, and even on scale melting at 124°, gave in *Graefe's* test such indications as would point to the presence of ceresin.

Kantorowicz[3] dissolves 1 grm. of the sample in 100 c.c. of boiling propyl acetate under a reflux condenser. After cooling the solution to 30° C. and allowing to stand at that temperature for 10 minutes, the precipitated ceresin is filtered off, pressed, and after drying at 105° C., weighed. The dissolved paraffin wax may also be recovered from the filtrate.

Berlinerblau[4] suggested, as a means of detecting admixture of paraffin wax to ceresin, the refractometric examinations of a suspected sample, or of fractions thereof. Following up this suggestion, *Ulzer and Sommer*[5] thought that paraffin wax might thus be differentiated from ceresin. According to their observations, ceresin shows a refraction of 11·5-13 "degrees" in the butyro-refractometer at 90° C., as against 1·5-6·8 "degrees" for paraffin wax (and 15 "degrees" for montanwax). It is obvious that a "rapid method" of this kind must be useless under the particular circumstances, especially as no guarantee was given for the purity of the ceresin employed. Moreover, the limits stated by the last-named observers are far too narrow, as the following observations by *R. Berg*[6] prove :—

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[1] *Chem. Zeit.*, 1903, 298.
[2] *Ibid.*, 1903, 408.
[3] *Ibid.*, 1913, 1566.
[4] *V. International Congr. for Appl. Chem.* Berlin, vol. ii. 625, 1904.
[5] *Chem. Zeit.*, 1906, 142.
[6] *Ibid.*, 1903, 755.

Butyro-refractometer "Degrees" of Paraffin Waxes
(Observed at 84° C. calculated to 40° C.)

	Melting Point. °C.	"Degrees."
Soft paraffin	36-38	23·6-23·8
" "	40-42	23·7-24·2
" "	43-44	24·6-25·3
" "	45-46	25·1-26·9
" "	47-49	27·3-28·1
" "	50-52	28·6-29·0
" "	59-60	30·0-30·8
"Scale"	44-48	26·2-27·0
Hard paraffin, Saxo-Thuringian	50-51	27·9-28·4
" " " "	52-53	28·9-30·5
" " " "	59-60	30·0-30·8
" " Javanese	50-51	28·0-28·5
" " American	52-53	28·2-30·4

Butyro-refractometer "Degrees" of Ceresin
(Observed at 84° C. calculated to 40° C.)

Melting Point, ° C.	"Degrees."
57-58	32·2-32·6
59-61	32·3-33·3
66-68	35·2-41·7
69-70	35·3-42·2
71-73	35·5-42·2

Berg's original observations at 84° C. have not been recorded. In order to obtain numbers which can be compared with the preceding and the following observations, I have calculated *Berg's* numbers to a temperature of 90° C., using as a factor 0·55 per degree centigrade. Provided this factor be correct, the following would be the calculated *minima* and *maxima* :—

	"Degrees," Minima and Maxima.	
	At 40° C.	Calculated to 90° C.
Hard paraffin waxes	27·9-30·8	0·4- 3·3
Ceresin	32·2-42·2	4·6-14·7

Higher numbers have been observed by *Marcusson and Schlüter*[1] for ceresins, as is indicated by the following table :—

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[1] *Chem. Zeit.*, 1907, 348.

	Melting Point in Capillary Tube. ° C.	Butyro-refractometer at 90° C. "Degrees" (calculated).
Paraffin wax, Saxo-Thuringian .	55·0-56·0	0·6
,, ,, ,, ,, .	51·0-54·0	0·0
,, ,, Scotch . . .	49·0-54·0	0·0
,, ,, Galician . .	55·0-57·0	3·8
Ceresin prepared in the laboratory from ozokerite . .	67·0-69·0	13·8
	68·0-69·0	13·8
	64·5-65·5	12·3
Commercial ceresins guaranteed pure, ten samples . . .	62·0-76·5	12·1
	72·0	14·2
	67·0-70·0	17·7
	67·5-70·0	12·6
	69·0-73·0	15·0
	77·0	14·5
	83·0-84·0	17·1
	70·0-72·0	15·8
	69·0-70·0	15·8
	58·0-76·0	14·9
Commercial ceresin, origin unknown	71·0	17·8

Marcusson and Schlüter rightly point out that a mixture of 60 per cent of ceresin having a refraction of 17·1-17·8 "degrees," with 40 per cent of paraffin wax, would show a refraction of 12·2 "degrees," and would have to be declared as pure ceresin, if *Ulzer and Sommers'* limits were to be taken as a guide.

Marcusson and Schlüter base a method for detecting paraffin wax in ceresin on *Graefe's* process, described above. They proceed as follows :—3 grms. of the sample, freed from rosin and any saponifiable substances, are dissolved in 30 c.c. of carbon bisulphide by gently warming under a reflux condenser. The solution is cooled in a water-bath to 25° C. and mixed with 300 c.c. of a solution prepared from equal parts of 96 per cent (by volume) alcohol and ether. The precipitate obtained thereby is filtered rapidly on a *Büchner* filter, washed with 25 c.c. of the alcohol-ether mixture at 20° C., and transferred, with the aid of warm benzene, into a tared dish ; the solvent is evaporated, and the residue weighed. The percentage of paraffin wax, p, is calculated from the amount of precipitate weighed, a, by the following formula :—

$$p = 100 - \frac{(100 \times a)}{60} \div 60 + \frac{3}{5}(60 - a),$$

the assumption being made that pure ceresin yields 60 per cent of precipitate under the above conditions, whilst paraffin waxes of every description remain dissolved in the carbon bisulphide. The authors conclude that when the precipitate at 25° C. is less than 50 per cent of the original substance, then the sample must be regarded as adulterated, whereas if 55 per cent or more is found, it may be judged to be pure. In case amounts lying between 50 and 55 per cent be found, further tests are stated to be required. By distilling off part of the solvent and cooling the residual liquid, a precipitate is obtained which is passed twice more through the same process ; thus altogether four precipitates are obtained. The crystalline structure and the refraction of all four precipitates are then examined. In the presence of paraffin wax the final precipitates are crystalline, and their appearance is distinguishable from the slightly crystalline appearance of the final precipitates obtained from pure ceresin. If the sample consisted of a mixture of ceresin and paraffin wax, then the refraction decreases in a marked degree from the first to the second precipitate, whereas in the case of pure ceresin a gradual decrease only is noticeable. Thus a pure ceresin with a refraction of 13·8 "degrees" gave a first precipitate having a refraction of 14·6 "degrees," and a second precipitate with a refraction of 11; whereas a "ceresin" containing 50 per cent of paraffin wax of the refraction of 7·5 yielded by the above method a first precipitate having a refraction of 16·7 "degrees," and a second one with a refraction of 6·9. The amounts of first precipitates obtained in the case of pure ceresins were found to be approximately the same, even when the original substances showed wide differences as regards melting point and refraction. Thus two ceresins melting at 67°-70° C. and 83°-84° C. respectively gave at 20° C. (at which temperature a larger amount of precipitate is obtained than at 25° C.) 64 and 61 per cent respectively of insoluble substances, and two other ceresins having the refraction of 12·6 and 17·8 "degrees" yielded 66 and 67 per cent respectively at 20° C.

Holde and Franck[1] use the following modification of *Graefe's* method:—1 grm. of the sample dissolved in 50 c.c. of chloroform is mixed with 60 c.c. of 96 per cent (by volume) alcohol. The precipitate is filtered off on a *Büchner* filter, the solution is evaporated and the residue dissolved in 5 c.c. chloroform and treated with 15 c.c. of 96 per cent alcohol. The second precipitate is filtered as before and the solution evaporated. By these means three fractions are obtained for which *Holde and Franck* give the following figures:—

	First Precipitate.		Second Precipitate.		Unprecipitated Residue.	
	R.	Amount.	R.	Amount.	R.	Amount.
Ceresin 1, yellow, soft	15·4	79·2	8·0	6·7	28·3	10·8
Ceresin 1, with 10 per cent paraffin wax, m. p. 50°-51° C.	14·5	75·3	4·6	7·5	23·0 (freed from oil +0·6)	12·4
Ceresin 1, with 15 per cent paraffin wax, m. p. 50°-51° C.	14·6	75·9	2·8	7·5	17·2 (freed from oil +1·0)	13·0
Ceresin 2, white	13·8	81·3	5·7	8·6	12·3	8·2
Ceresin 2, with 10 per cent paraffin wax	11·9	74·6	2·5	7·5	7·1 (freed from oil −1·0)	11·0

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[1] *Petroleum*, 1914, 669. Cp. also Holde, *Chem. Revue*, 1914, 86.

It would appear from the foregoing notes that a reliable method of analysing ceresin is still a desideratum, as small quantities of added paraffin wax, from 10 to 20 per cent, cannot be detected with certainty. *Marcusson and Schlüter's* method will, however, be instrumental in stemming the adulteration of ceresin, which has been practised to such an extent that the belief has gained ground that pure ceresin is unobtainable in commerce. In fact, every candle-maker buys only according to sample, which he tests by his own practical methods as to suitability for his purposes.

Although ceresin is largely used in the candle industry for stiffening the wicks of night-lights, it is not very suitable for the production of candles, not only because those made from pure ceresin smoke persistently, but also because ceresin candles cannot be moulded in machines with the same facility as are stearine and paraffin wax candles, the ceresin candles being very apt to adhere to the mould and to exhibit cavities in the solidified mass. To prepare ceresin candles, as is done in some Continental works, the material is preferably " drawn " in a similar manner to that employed in the manufacture of beeswax candles (see below). Latterly, ceresin candles are also moulded in special moulds, great care being exercised in observing the temperature of both candle material and moulds when pouring and when allowing to cool. Such " ceresin " candles contain throughout some paraffin wax, so as to " correct " the refractory behaviour of pure ceresin. In hardness and in illuminating power ceresin candles considerably surpass paraffin wax candles.

Ceresin is further used to a great extent as a constituent of " wood fillers " and " floor polishes " (see " Technology of Waxes ") ; it has also been proposed as a constituent of anti-fouling and anti-rusting paints (to replace effectively tar), and of " vaseline." [1]

(γ) MONTANWAX—LIGNITE WAX

French—*Cire de lignite.* German—*Montanwachs, Braunkohlenwachs.*
Italian—*Cera di lignite.*

Montanwax was first prepared (*E. von Boyen* [2]) from the bitumen extracted from dried Thuringian lignite by means of volatile solvents.[3] A specimen of the " crude wax " examined in the laboratory melted at from 80° to 86° C. It is easily soluble in hot petroleum ether and in carbon tetrachloride, but is *not completely dissolved by hot ether* or boiling alcohol.

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[1] Cp. also J. Girard and P. J. Tabourin, French patent 337,753 ; cp. also French patent 326,348.

[2] German patents 101,373, 116,453 ; United States patent 1,092,629 ; *Zeits. f. angew. Chem.*, 1899, 64 ; 1901, 1110. Cp. also French patent 338,736 by E. Bouchaud-Praceig, who proposes to extract the " wax " from lignite and peat by means of alcohol and ether. For vulcanised bitumen cp. English patent 21,742, 1907 (S. Paterson).

[3] H. Köhler proposes the employment of naphthalene for extracting the bitumen, German patent 204,256.

On being distilled with superheated steam, after having been freed from the solvent, this bitumen yields under ordinary pressure a white hard mass, melting above 70° C., and consisting of a mixture of fatty acids and a hydrocarbon. The acid, "montanic acid," melts at 80° C., and has the specific gravity 0·915. The hydrocarbon is a saturated compound of the specific gravity 0·920, and crystallises from benzene in shining white laminæ, melting at 60·5° C. On heating with concentrated sulphuric acid the hydrocarbon is readily carbonised (difference from paraffin wax).

This hydrocarbon appears to be a product of decomposition, for on distilling the extracted bitumen with superheated steam *in vacuo* the then resulting product consists of montanic acid and of an alcohol. This would point to the bitumen being a true wax [1] (in the chemical sense). The wax is hydrolysed by superheated steam, and its constituents distil over in the uncombined state. The alcohol is separated from the acid by pressing in the hot. The acid is then decolorised by treatment with charcoal, etc.

The still residues—montan pitch, ebonite wax—are (like "stearine pitch") used for insulating purposes and in the manufacture of gramophone cylinders.

Another patented method [2] of purifying the crude bitumen consisted in melting together 30 parts of crude bitumen with 70 parts of paraffin wax and treating the mixture with 10 to 20 per cent of sulphuric acid of 66° Bé. (or a still more concentrated acid) at 160° to 200° C., until all water, sulphurous acid, and other volatile substances have been driven off completely. The resulting product was then decolorised by means of char. It was stated by the patentee that the added paraffin wax could be removed by hot pressing. Another process [3] claims purification of the crude bitumen by treating it with nitric acid of specific gravity 1·2 to 1·4 in the hot until most of the acid has volatilised, washing to remove the mineral acid and separating the dark resinous mass from the refined bitumen by filtration. The production of the aluminium salts of montanic acid has been patented.[4]

A sample of "montanwax" examined in the author's laboratory had the following characteristics:—

Melting point	80° C.
Neutralisation value	123·01
Unsaponifiable matter in neutralised mass	6·40 per cent
Saponification value	126·58
Unsaponifiable in saponified mass	3·58 per cent

According to *Hell*,[5] montanic acid [6] has the formula $C_{29}H_{58}O_2$, and melts at 84° C. This, however, has been shown by *Rigg* to be a mixture of cerotic, montanic, and melissic acids, montanic acid having the formula $C_{28}H_{56}O_2$ (cp. Vol. I. p. 174). On calculating the neutralisation and saponification numbers found in the author's laboratory to $C_{28}H_{56}O_2$, the following would appear to be the composition of montanwax :—

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[1] Cp. J. Marcusson and H. Smelkus, *Chem. Zeit.*, 1917 (41), 129, 150.

[2] Ernst Schliemann's Export-Ceresin-Fabrik, German patent 202,909; English patent 22,500, 1910; Wachs- u. Ceresin-Werke, J. Schlickum and Co., German patent 254,701; Montanwachs-Fabrik, German patents 216,281, 260,697; Nathanson, German patent 200,050.

[3] German patent 207,488 (Th. Asher); Wachs- u. Ceresin-Werke, J. Schlickum, German patents 237,012, 247,357.

[4] Schliemann's Export Ceresin Fabrik, G.m.b.H., German patent 221,888.

[5] *Zeits. f. angew. Chem.*, 1900, 556.

[6] "Geoceric acid" (Kraemer and Spilker, *Berichte*, 1902, 1217).

	From Neutralisation Value.	From Saponification Value.
	Per cent.	Per cent.
Acid	92·96	95·66
Unsaponifiable . . .	6·4	3·58
	99·36	99·24

From these numbers it may be gathered that the product still contains some undecomposed "wax." As in each case there is a constant difference of about 0·7 per cent the conclusion must be drawn that there was present in the sample a small quantity of an acid having a higher molecular weight than montanic acid.

The composition of commercial montanwax has been changed since the above detailed examination was made by the author. This will be gathered from the following table :—

	"Montana" Wax.[1]	Montanwax.[2]
Melting point, ° C.	76	77
Acid value	73·3	93·02
Saponification value . . .	73·9	94·56
Iodine value	16	12·00
Unsaponifiable matter, per cent .	47	28·89

From each of the samples "montanic acid" of the melting point 83° C. was isolated. The unsaponifiable matter of "Montana" wax crystallises from hot benzene in needles, melting at 58°-59° C. and having the specific gravity of 0·92 ; it is very sparingly soluble in cold alcohol and ether, slightly soluble in chloroform and petroleum ether and dissolves readily in the hot solvents. The unsaponifiable matter differs from saturated hydrocarbons in that it dissolves easily in hot absolute alcohol. The unsaponifiable portion does not appear to be an alcohol, inasmuch as an acetyl derivative could not be obtained by heating with acetic anhydride ;[1] nor could it be converted by heating with potash lime into an acid.[1] Another commercial product, *montanin*[1] *wax* appears to have been obtained from montanwax by neutralising a portion of the free acid with sodium hydrate. The analysis indicated that the product consisted of 41·3 per cent of montanic acid, 23·9 per cent of the sodium salt of the same acid, and 34·8 per cent of unsaponifiable matter. By the partial neutralisation of the free acid, the melting point of the product had been raised to 95°-97° C. A sample of montanwax examined by *Grun and Ulbrecht*[1] consisted of 66 per cent of montanic acid and 34 per cent of unsaponifiable matter which was identified as montanone melting at 59·6° C.

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[1] Ryan and Dillon, *Proceedings of the Royal Dublin Society*, 1909, 202.

[2] Eisenreich, *Chem. Revue*, 1909, 211.

It would appear that Irish lignite yields a similar substance.[2]

Whereas *Engler*[3] stated that montanwax in a 1·5 per cent chloroform (or picoline) solution does not exhibit optical rotation, *Walden*[4] found for a crude bitumen obtained from lignite by extraction with benzene, and which was then again extracted with absolute alcohol, the specific rotation $[a]_D = +10°$. On distilling the bitumen *in vacuo* *Walden* obtained a yellow oil of buttery consistence which furnished, after recrystallisation from alcohol, snow-white crystals, melting at 61° to 62° C. and exhibiting slight rotation in chloroform solution. On heating montanic acid with iron filings *Easterfield and Taylor*[5] obtained "montanone" of the formula $(C_{27}H_{55})_2O$.

This product was at first proposed as a candle material, but extended experience has shown that it is useless for this purpose, especially as it produces a smoking flame. As a "candle stiffener" it is greatly inferior to carnaüba wax. The "German method" (p. 274) of determining the melting point led to the erroneous view that montanwax raises the melting point of paraffin wax or "stearine," with which it is admixed. When the melting points of mixtures of paraffin wax and montanwax are determined by *Shukoff's* method, they are found to be lower than is indicated by calculation (cp. Vol. I. Chap. III.). Montanwax is chiefly used in the manufacture of polishes (see "Technology of Waxes"), as a substitute for carnaüba wax and as an insulating material in place of ceresin. Its admixture with tar for waterproofing roofs, etc., has been patented by *Schmidt & Co.*;[6] it also finds a use as material for the production of gramophone records.

Nearly related to montanwax appear to be "Sea-weed Wax" ("Wax from Algæ") and "Peat Wax."

Sea-weed wax (*wax from Algae*) (French—*cire de fucus*. German—*Algenwachs*. Italian—*cera di alga*) is obtained from marine deposits of *algae*, which are known in Germany as "Seeschlick," and are found in large quantities in the peat-bogs of North Germany. This wax[7] appears to consist of arachidic, behenic, and lignoceric acids, combined with higher alcohols containing in the molecule 20 to 22 atoms of carbon.

In the opinion of *Kraemer* this wax is the mother substance of petroleum,[8] and the naphthenic acids occurring in petroleum would represent acidic decomposition products of the wax.

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[1] *Zeits. f. angew. Chem.*, 1916 (29), 371.

[2] Ryan and Dillon, *Proceedings of the Royal Dublin Society*, 1909, 202.

[3] *Chem. Zeit.*, 1906, 711.

[4] *Ibid.*, 1906, 1167.

[5] *Journ. Chem. Soc.*, 1911, 2302.

[6] German patent 222,768.

[7] Kraemer and Spilker, *Berichte*, 1889, 2940; 1902, 1212.

[8] *Chem. Zeit.*, 1907, 675.

Peat Wax (French—*cire de tourbe.* German—*Torfwachs.* Italian —*cera di torba*).—By extracting peat with alcohol *Zaloziecki and Hausamann*[1] obtained a wax-like substance[2] which was resolved by means of ether into two components. The more readily soluble, dark green "wax," the odour of which is similar to that of beeswax, yielded on saponification with caustic soda an acid melting at 184° C. and showing the composition $C_{17}H_{25}O_5$, and an alcohol, melting from 124° to 130° C., having the composition $C_{20}H_{40}O_4$. The second substance, which is more sparingly soluble in alcohol, furnished on saponification the same alcohol, whilst the acid which was combined with it has probably the composition $C_{21}H_{35}O_7$; this acid did not melt at 260° C.

The production of wax from peat has been patented by *Bouchard-Praceig.*

The selection of suitable candle material or mixtures of candle materials for every given purpose, and the selection of wick for these require special experience. Thus a candle material having too low a melting point will cause guttering and bending of the candle, whereas a candle of too high a melting point will burn with an outer "cup," inasmuch as the supply of melted material is not sufficiently plentiful to keep up the burning.

Schauermann[3] patents the incorporation of chalk and (or) casein to the candle material.

Candles giving a coloured light are prepared by incorporating metallic salts with the candle material; in especial, monochromatic candles for photographic purposes are prepared by the addition of strontium nitrate. *Scheuble*[4] states that it is first necessary to prepare a candle giving a very slightly luminous flame, and proposes for this the use of amino or imino acids and their esters, with the addition of an oxygen yielding salt, such as ammonium nitrate, to ensure combustion.

The finished candle material is made into candles by melting and moulding it in the well-known candle machines. These machines are in outer appearance similar to the soap-cooling machine shown in Fig. 23. Like the latter, they are supplied with hot and cold water, but carry in addition at the lower part the wick bobbins which supply the wick to the candle material.

These machines work discontinuously; after the material has been poured into the mould the candles are allowed to solidify, and are then taken out by hand. A continuous candle machine has been constructed by *Fournier and Company.*[5] This machine appears to be somewhat complicated, although it may commend itself to large candle-works which suffer from shortage of water. A description of candle machines and of the various forms of moulds for self-fitting, hollow, and other candles falls outside the scope of this work, and may be omitted all the more readily, as all candle machine makers supply catalogues containing excellent illustrations and full descriptions, and setting out in detail the advantages of their machines.[1] Nor does the full description of the preparation of candle wicks come within the purview of this work. It need therefore only be pointed out briefly that the preparation of the wick is of great importance in order to ensure the proper burning of a candle, each candle material requiring a wick of different thickness so as to prevent "guttering" on the one hand, and burning with a smoky flame on the other. Paraffin wax candles require a thinner wick than beeswax or stearin in order to retard the supply of oil to the flame. The wicks are made of best cotton,[2] and are plaited (*Cambacères* in 1825), so that they curl and bend outside the flame, where the cotton can burn away completely. Before being put into the candle machine the wick undergoes "pickling," the object of this process being to retard the too rapid combustion of the cotton and at the same time to vitrify it slightly when it protrudes from the flame, so that the ash may drop off readily. By the use of a combination of combustible fibres and metallic filaments *Scheuble and Hochstetter*[3] claim to be able to produce a wick which bends uniformly as the candle burns. The composition of "pickling" solutions used to be guarded as a valuable secret, and each maker had his own recipe, specially adapted to his own candle material. Most of the pickling solutions contain borax, or phosphate of ammonia, or potassium nitrate, or similarly acting salts.[4] The wick is prepared by steeping the plaited material in the pickling solution. The excess of the latter is removed in a centrifugal machine, and the hanks are then dried in a stove or hot air chamber, and finally wound on to the bobbins.

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[1] French patent 338,736.

[2] *Zeits. f. angew. Chem.*, 1907, 1141.

[3] English patent 12,331, 1909.

[4] German patents 216,338, 234,340.

[5] *Engineering*, 1901, February 1; cp. Dresco, German patent, 253,048.

In order to ensure the ready lighting of a candle *Haase*[5] impregnates the protruding end of the wick with a solution of celluloid in acetone. *Ohlsson*[6] attempts to reach the same object by a mechanical arrangement in so shaping the mould that the end of the wick is saturated with the candle material.

The finished candles are cut,[7] washed, polished, branded by machinery, and bleached by exposure to light before being packed.

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[1] With regard to moulds made from porcelain and similar material, cp. German patent 195,702 (V. Lewy); French patent 396,744.

[2] Wicks made of paper have been patented by S. Funke, German patent 195,822. Wicks containing a wire of easily fusible and combustible metal (especially for hollow candles) have been patented by Varenkamp (German patent 108,341). This patent is an imitation of an older patent of Palmer, who introduced into the wick a thread coated with bismuth.

[3] German patent 244,358.

[4] Esche, French patent 324,739, patents a "pickling" solution consisting of sodium silicate, sodium thiosulphate, and ammonium bichromate. The dried wick is then finally coated with Japan wax.

[5] German patent 158,928; French patent 342,527; Calderwood and Webb, English patent 26,955, 1910.

[6] German patent 150,916.

[7] Pouleur and Kojewnikow, German patent 205 784.

In order to render candles non-transparent some manufacturers incorporate with the paraffin wax a small amount of white lead.

The chemical examination embraces a number of tests which have already been referred to incidentally under the description of the different candle materials enumerated above (cp. p. 262). Further tests to which the finished candles are subjected are " bending tests " (" stability tests "), and tests as to the length of time a candle is expected to burn (especially in the case of night-lights). Details of these tests are generally laid down in specifications between buyer and seller.

The determination of the illuminating power (candle power) of a given candle falls outside the scope of this work (cp. also " Sperm Candles," below). It must therefore suffice to reproduce here a few numbers taken from a table by *Lockemann*[1]:—

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[1] *Zeits. f. angew. Chem.*, 1906, 1763.

	Spherical Candle Power.	Hourly Consumption of Material.		Heat developed per Hour.		Carbonic Acid produced per Hour.		Comparative Cost of Candle Material.	Light in "Hefner Candle" obtained for One Shilling.
	"Hefner Candles."	Total.	Per "Hefner Candle."	Total.	Per "Hefner Candle."	Total.	Per "Hefner Candle."		
		Grms.	Grms.	Kilogram-Calories.		Litres.	Litres.	Shillings per Kilo.[1]	
Beeswax candle . .	1·00	6·90	6·90	65	65	11·1	11·1	5·00	29
Stearine ,, . .	1·09	8·58	7·80	75	69	12·9	11·9	1·60	79
Paraffin wax candle . .	1·35	8·47	6·27	87	64	14·5	10·7	1·20	117
Composite ,, . . (consisting of two parts of paraffin and one part of stearine)	1·23	8·54	6·94	81	66	13·9	11·4	1·40	103
Rape oil lamp, loose wick .	0·8	7·62	9·53	72	90	11·4	14·3	0·80	131

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[1] These figures are, of course, subject to market fluctuations, but are sufficiently accurate for purposes of comparison.

An inquiry made by the author in 1903 respecting the annual consumption of candle material in this country led to an estimated quantity of 45,600 tons, which may be distributed over the different materials described above as follows :—

Tallow	1,000 tons
"Stearine"	2,190 "
Paraffin wax	42,200 "
Ceresin	100 "
	45,490 tons.[1]

In the Saxo-Thuringian candle industry about 8000 tons of paraffin wax are consumed annually ; to this may be added about 20 per cent of "stearine" used as a "stiffener." Further general statistical data on which any reliance could be placed are not obtainable. The following table, however, shows the imports into France of candles and candle material :—

	1912.	1913.	1914.	1915.	1916.
	Kilograms.	Kilograms.	Kilograms.	Kilograms.	Kilograms.
Candles	262,800	200,500	148,500	1,067,600	2,625,700
"Stearic acid"	12,300	33,200	3,000	3,600	13,000

	1917.	1918.	1919.	1920.	1921.
	Kilograms.	Kilograms.	Kilograms.	Kilograms.	Kilograms.
Candles	2,371,300	232,600	18,928	15,952	318,800
"Stearic acid"	4,800	2,200	10,000	3,400	2,500

II. FATTY ACID INDUSTRY

The *solid fatty acids* prepared in the arts consist almost exclusively of a mixture of stearic and palmitic acids, the manufacture of which has been described fully in the preceding section. The bulk of the "stearine" finds its employment in the candle industry ; only small quantities are used in other industries, as in the making of polishes (see below), of waterproofing preparations,[2] phonograph records, copying ribbons and papers [3] and as an adulterant of beeswax. Lower qualities of "stearine," such as are obtained from "Waste Fats" (Chapter XVI.), are used for soap-making purposes, etc., for which the "stearine" described above would be too expensive. This applies especially to those stearines which contain notable amounts of unsaponifiable matter.

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[1] Spermaceti candles, 50 tons ; beeswax candles, 60 tons.

[2] Hübner and Riley and Co., Ltd., English patent 7972, 1908 ; Plüss, German patent 255,354.

[3] Cp. German patents 170,820, 171,999 ; 223,031, 237,772 ; Gottschalk, German patent 233,474 ; Badische Anilin und Soda Fabrik, German patent 252,052.

The preparation of other *solid* fatty acids belonging to the saturated series has been described in Vol. I. Chap. III., but none of them is prepared on a commercial scale, as no demand has arisen hitherto, although there appears to be a wide field open for their application in the arts.[1] Under the name " Sabromine " the calcium salt of dibromobehenic acid obtained by the action of bromine on erucic acid is used in medicine.

The *lower* fatty acids from butyric upwards are used as such (cp. butyric acid in margarine manufacture, p. 37) to a very small extent only. A patent for their preparation, particularly that of butyric acid, has been taken out by *Soc. d'Étude du Carburx.*[2] Larger quantities of those acids are used in the form of esters as flavouring essences. A description of the processes employed for the preparation of such essences falls outside the scope of this work, and it need only be mentioned that for their preparation *Haller*[3] treats glycerides containing notable amounts of lower fatty acids, such as coconut oil and palm kernel oil, with a methyl- or ethyl-alcoholic solution of hydrochloric acid (" alcoholysis "), and interrupts the process of saponification when the methyl or ethyl esters of the lower glycerides have been formed; these are then separated off and used for purposes of perfumery and confectionery. The same object is protected in a patent specification by *Winter*,[4] who saponifies coconut and palm nut oils to an extent of 90 per cent only, and then fractionates the product with superheated steam *in vacuo* (cp. p. 238). His *modus operandi* may be illustrated by the following data :—

Fraction.	Temperature.	Vacuum.	Yield.
	°C.	mm.	Per cent.
First	220-222	50-100	50
Second	222-240	50-100	40
Residue, neutral fat, tarry matter	...	...	10

The recent shortage of fatty acids for soap-making purposes led to renewed efforts to prepare them by the oxidation of hydrocarbons. Some measure of success was obtained in the small scale experiments. In Germany it is even claimed that the process is feasible on a commercial scale, although in view of the extreme difficulty in controlling the process of oxidation this is doubtful. The action of the usual oxidising agents was investigated by *A. Langer*[5] although the more usual procedure was to use air or oxygen preferably under pressure and in the presence of a metallic catalyst.

C. Gränacher[6] uses air containing nitrogen peroxide. The fatty acids so prepared are in general dark brown salve-like bodies having neutralisation values ranging from 150 to 360, the higher value being obtained by prolonging the time of oxidation. The yield obtained rarely exceeds 70 per cent, the acids when formed being broken down into bodies of low molecular weight which are soluble in water. For the details of various processes produced the papers given in the footnote[1] should be consulted. The production of fatty acids from montanwax by means of ozone has been patented.[2]

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[1] Cp. Bonnet, English patent 21,068, 1900; German patent 124,237.

[2] French patent 469,552.

[3] French patent 361,552.

[4] German patent 170,563.

[5] *Chem. Zeit.*, 1921 (45), 466.

[6] *Helv. Chim. Acta*, 1920 (3), 721.

The most important of all the *liquid fatty acids*, from a technical point of view, is oleic acid, which will be described below. The method for preparing other liquid fatty acids has been given in Vol. I. Chap. III., but hitherto these have not yet found extensive application in the arts, although to them also a wide field lies open. Attempts have been made to use them as solvents; thus the fatty acids of linseed oil, tung oil, and castor oil are proposed, at temperatures above 300° C., as solvents of keratin[3] (waste scraps of horn) and casein. Linseed oil fatty acids are used as a solvent for copal gums (without previous melting) in the manufacture of varnishes.[4]

With regard to the technical application of "ricinoleic acid" cp. "Wool Oils" (p. 113). Fatty acids prepared from fish oils require deodorising before use.[5]

Besides *oleic acid*, this section deals with "Soap Stock Fatty Acids" and "Derivatives of Fatty Acids" made on a commercial scale.

1. Oleic Acid, Oleine, Elaine, Commercial Oleic Acid

French—*Acide oléique.* German—*Ölsäure, Ölein, Elaïn.*
Italian—*Acido oleico, oleina.*

Commercial oleic acid is a by-product of the candle industry; and, as has been pointed out already, it is obtained in two qualities, viz. "saponification oleine" and "distillation oleine."

Saponification oleine[6] is usually of dark colour, and unless carefully freed from "stearine" by refrigeration, contains considerable quantities of solid fatty acids. Hence, the iodine value of such oleine lies much below 90 (cp. Vol. I. Chap. I.). All the neutral fat which has escaped hydrolysis in the autoclave processes is found in this oleic acid. Hence, its saponification value is higher than its neutralisation value.

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[1] W. Schrauth, German patent 327,048, 1914; C. Harries, R. Koetschauand, E. Albrecht, German patent 332,478, 1916; A. Schmidt, English patent 109,386, 1917; C. Harries, German patent 339,562, 1919; W. Schneider, *Brennstoff Chem.*, 1920 (1), 70, 80; A. Schmidt, English patent 142,507, 1920; G. Teichner, English patent 148,358, 1920; Deutsche Erdöl, English patent 148,892, 1920; K. Loffl, *Chem. Zeit.*, 1920 (44), 561; A. Schaarschmidt, and M. Thiele, *Berichte*, 1920 (53), 2128; A. Grun and T. Wirth, *Zeits. f. angew. Chem.*, 1920 (33), 291; W. Schneider and A. Jantsch, *Chem. Zentrl.*, 1921 (92), ii. 379; W. Schneider, *ibid.*, 1921 (92), ii. 376, 378; F. Fischer and W. Schneider, *ibid.*, 1921 (92), ii. 376, 377, 522; F. Fischer, *ibid.*, 1921 (92), ii. 377; *Journ. Soc. Chem. Ind.*, 1921, 62 R.

[2] F. Fischer and H. Tropsch, German patent 346,362.

[3] German patents 191,552; 224,501 (S. Diesser).

[4] Livache, *Compt. rend.*, 1908, 898.

[5] Böhm, German patent 230,123.

[6] In Austria "oleine" from the cold presses is sold as "saponification oleine, pure," to differentiate it from oleine obtained from the hot presses, which is sold as "saponification oleine, commercial (ordinary)."

All the unsaponifiable matter contained in the fats subjected to "autoclaving" is likewise found in the oleine.

Distillation oleine obtained by the sulphuric acid saponification process or by the "mixed process" is a distilled product, and hence represents a pale transparent oil. It usually contains small quantities of solid fatty acids, so that the iodine value of properly manufactured "distillation oleine" from tallow lies between 80 and 86.

Before the process of distilling fatty acids had reached its present state of perfection, large quantities of hydrocarbons (cp. p. 235) distilled over together with the oleine, in consequence of destructive distillation of neutral fat taking place in the still. It was then easy to distinguish "distillation oleine" from "saponification oleine" by the presence of hydrocarbons in the former. At present, however, the manufacturing processes are carried out in such a manner that the distillation oleines of commerce are practically free from products of decomposition.[1]

The following table contains a few analyses of typical "oleines" as obtained in the saponification of fats :—

Analysis of Commercial Oleines (*Lewkowitsch*)

Commercial Oleine from	Consistence.	Colour.	Free Fatty Acids.	Unsaponifiable.	Neutral Fat.		Iodine Value.
					Direct.	By Difference.	
			Per cent.	Per cent.	Per cent.	Per cent.	
Tallow by autoclave process	Fluid, with slight deposit	Dark brown	88·2	...	11·5	...	80
Tallow and palm oil by autoclave process . .	Clear liquid	Dark brown	86·6	...	14·0	...	...
Tallow and palm oil by lime saponification . . .	,, ,,	Pale brown	94·6	2·6	3·4	...	...
					Lactones.		
Tallow and palm oil by acid saponification . . .	Clear liquid	Pale brown	92·2	3·2	...	5·6	...
Tallow and palm oil by acid saponification . . .	Solid at 15° C.	White	97·8	1·0	...	1·2	...
Tallow by acidification, twice distilled . .	...	,,	96·9	...	3·0	3·1	81·3
Tallow and palm oil by acidification, twice distilled	...	,,	94·5	4·02	...	1·3	82·3

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[1] In order to avoid the formation of hydrocarbons when distilling fatty acids (especially those from acidification processes) Dreymann (English patent 10,466, 1904; French patent 343,158; German patent 164,154) converts the fatty acids into their methyl or ethyl esters (see Vol. I. Chap. XII.), and distils the esters in a current of steam *in vacuo*. The esters are then saponified in autoclaves so as to regenerate the fatty acids and to recover the alcohol. It appears to the author very unlikely that a process of this kind will ever be carried out on a large scale, as the cost would be prohibitive.

Other "oleines" obtained from waste products of the fat industries, and containing large proportions of unsaponifiable matter, have been described already under the headings: "Wool Oils" (Table, p. 109), and "Distilled Oleines from Recovered Grease" (p. 109). An exhaustive examination of "oleine" of the latter kind has been given by way of example in Vol. I. Chap. XI. (cp. also Chap. XVI.).

For further information on oleines from waste fats, such as "Cotton Seed Foots," the reader is referred to Chapter XVI.

In an oleine intended for the manufacture of soap the unsaponifiable matter only need be determined, a certain proportion of solid fatty acids or of neutral fat being rather desirable than otherwise. For the rapid valuation of saponification oleine, intended for soap-making, it suffices to saponify with alcoholic potash, and divide the saponification value found [1] by 2, when the percentage of saponifiable fat is obtained with sufficient accuracy. If it be required to ascertain whether a sample of saponification oleine has been obtained from tallow only, or from a mixture of tallow with a vegetable fat, the phytosteryl acetate test (Vol. I. Chap. IX.) will give the readiest answer.

Saponification oleine, which is too dark for certain commercial purposes (*e.g.* pale soap), can be "bleached" successfully (cp. Vol. II. Chap. XIII.).

In the examination of distilled oleine the proportion of unsaponifiable matter is best determined direct. Its amount furnishes a guide as to the care with which the product has been manufactured. The data given in the foregoing table supply the necessary guidance.

"Distilled grease oleine" in best "distillation oleine" is detected by means of the cholesterol and isocholesterol reactions, as also by the presence of a notable proportion of unsaponifiable matter.

The methods proposed for the partial or complete conversion of oleic acid into solid material have been fully discussed above (p. 244).

The uses to which oleic acid is put have been incidentally pointed out in preceding sections of this chapter. It need therefore only be briefly repeated that oleine is used extensively as wool oil and in soap-making, especially for the manufacture of textile soaps and soap powders (dry soap); smaller quantities are employed in the preparation of metallic soaps (bismuth, copper, ferrous, ferric, lead, and mercuric oleates [2]) for pharmaceutical and technical purposes (cp. "Salts of the Alkaline Earths and Heavy Metals," below).

Germot and Rivière [3] claim the application of oleic acid for dissolving hard and semi-hard gums in the manufacture of varnishes. It should, however, be noted that oleic acid does not dissolve gum-resins.

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[1] Taking, for the purposes of rapid calculation, 200 as the neutralisation value of oleic acid.

[2] G. M. Beringer, *Amer. Journ. of Pharm.*, 1889 (61), 593; W. A. H. Naylor, *Pharm. Journ.*, 1901 (66), 392.

[3] French patent 159,635, 1884.

2. Soap Stock Fatty Acids

By the term "soap stock fatty acids" the author denotes those commercial fatty acids which are prepared on a large scale for the purposes of soap manufacturers. These differ essentially from the fatty acids obtained in candle-making processes, in that they contain considerable amounts of neutral fats, as a rule, from 10 to 20 per cent.

The industry dealing with these products has sprung up during the last decade since the successful recovery of glycerin from soap lyes in England, France, and the United States forcibly drew the attention of even small soap-makers in other countries to the waste of glycerin that was allowed to take place in soap-works. The manufacture of soap from oleic acid, the by-product of the candle industry, served as a model and as an inducement to attack on a commercial scale the frequently suggested proposal to hydrolyse ("deglycerinise") neutral fats in soap-works (with a view to recovering a richer glycerin than is obtained in the "salt crude glycerin," p. 379), and then to convert the resulting free fatty acids into soap by boiling them with caustic alkali or alkali carbonate, or, if necessary, with a mixture of both.

The following methods, differing as regards the principles which underlie the manufacturing processes, have been elaborated, and are now being carried out in practice :—

(1) Preparation of soap stock fatty acids by the autoclave process.
(2) Preparation of soap stock fatty acids by the *Twitchell* process.
(3) Preparation of soap stock fatty acids by the ferment process.

These processes would seem to belong to the domain of a soap-works. They are, however, largely carried out in separate establishments, where the chief object is to recover the glycerin, the fatty material being sold to small soap-makers, who are not in a position to undertake themselves the manufacturing operations involved in "deglycerinising."

(1) *Preparation of Soap Stock Fatty Acids by the Autoclave Process*

The practice of the candle industry showed that the higher the pressure at which the autoclaves are worked the more discoloured become the fatty acids, and especially the oleic acid, as most of the colouring substances remain dissolved in the expressed "oleine." The soaps made from autoclaved oleine were too dark to find favour with the public, and were therefore chiefly used for textile purposes.

Since the fatty material autoclaved at a pressure of 15 atmospheres yielded too dark a material to be converted into saleable household soap, and even material obtained at a pressure of 8 atmospheres (using a certain amount of lime, magnesia, zinc oxide, cp. p. 220) gave "off-coloured" products, a compromise was made between the process of the candle-maker and the customary process of the soap-maker (p. 315) by hydrolysing the oils and fats required by the soap-maker with the assistance of bases (cp. p. 220) in an autoclave at an even lower pressure. Thus it was hoped to prevent discoloration of the fatty material.

A process of this kind was patented by *Dangoise* and the *Société générale Belge de Déglycérination*.[1] The patent claims as a novelty the introduction into the autoclave of a portion of the fatty matter and base resulting from a previous operation—in other words, a portion of the fatty mass (hydrolysed in the well-known manner at a pressure of 5 to 6 atmospheres) from a previous charge is left in the autoclave. Thus more rapid hydrolysis is induced at the outset by virtue of the emulsifying power of the once formed soap. As the base (catalyst), lime, with the addition of zinc and zinc oxide, is used.

From the table given, p. 227, it will be gathered that the bulk of the fat is hydrolysed during the first few hours, whilst the progress of saponification during the later hours is disproportionately slow. Thus the fatty acids first formed are exposed to high pressure during a long time, and changes occur which act injuriously on them with the production of " off-coloured " material. By reducing the pressure to 5-6 atmospheres, and by reducing simultaneously the time during which the autoclaving process is conducted, a less discoloured product is obtained. The theoretical explanations given in Vol. I. Chapter II. lead *a priori* to the conclusion that under these conditions hydrolysis must be far from complete. Indeed, most of the autoclaved soap stock fatty acids which the author has examined during recent years contained from 10 to 20 per cent of unsaponified fat. It may also be pointed out that, notwithstanding the introduction of zinc oxide (zinc dust), discoloration of the fatty acids could not be prevented. *G. Bottaro* patented [2] a process for decomposing lime soap by means of gaseous sulphurous acid at a temperature of 30°-40° C., with a view to bleaching the fatty acids as they separate (and also to obtain simultaneously a concentrated solution of glycerin).

Further information on this subject will be given below (p. 333).

(2) *Preparation of Soap Stock Fatty Acids by the Twitchell Process*

The *Twitchell* process of hydrolysing, described in Vol. I. Chap. II., has also been adopted for the manufacture of soap stock fatty acids. It has been pointed out already that the *Twitchell* process fatty acids readily darken on exposure to the air, and that it is therefore essential to exclude access of air as much as possible. This is all the more necessary in the preparation of soap stock fatty acids, and in this case contact with air must be still more rigorously prevented by passing steam over the fatty acids whilst they settle out. Furthermore, the full time required for the completion of the hydrolysis is not allowed in this case ; hence the amount of neutral fat in the product is much larger than in the material prepared for candle-making purposes. The necessity of preventing serious discoloration has led to the practice of reducing the quantity of the reagent to less than 1 per cent, as it was found that the larger the quantity of the sulpho-aromatic substance added the deeper coloured became the product. Both factors contribute materially to reducing the amount of free fatty acid formed and to leaving a correspondingly larger amount of neutral fat in the mass. The author found in commercial soap stock fatty acids made by this process from 14 to 20 per cent of neutral fat. It is claimed that the use of a *Twitchell* reagent prepared from reduced (hydrogenated) fatty acids leads to the production of fatty acids having a much improved colour.[1]

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[1] English patent 11,074, 1901 ; German patent 171,200.

[2] English patents 23,534, 1906 ; 23,663 ; German patent 211,969 ; United States patent 987,426 ; French patent 449,392 ; Italian patent 347/20/112,418.

With regard to the soaps obtained from this material cp. p. 336.

(3) *Preparation of Soap Stock Fatty Acids by the Ferment Process*

The theory of, and the principles underlying, this process have been explained fully in Vol. I. Chap. II. The original *modus operandi*,[2] in which ground castor seeds (together with their husks) were brought into an emulsion with oils (or fats) and water, slightly acidulated with acetic acid or acid salts, has been abandoned, as the formation of a most troublesome middle layer between the fatty and aqueous layers led to considerable losses of fatty matter and other concomitant drawbacks (low quality of glycerin, etc.). Even the use of decorticated seeds, although palliating the evil, did not remedy the inconveniences. The author's [3] suggestion, viz. to isolate the ferment itself, has been worked out to a manufacturing process by *Nicloux*,[4] who triturates decorticated castor seeds with castor or cotton seed oil, filters the mass through a fine silk gauze, and centrifuges the turbid oil so obtained. The residue remaining on the filter may be subjected again to the same process, but in practice (see below) it is thrown away as valueless. The turbid filtrate separates into three layers. The excess of oil forms the uppermost layer, the practically inactive aleuron grains and membranes fall to the bottom, whilst the cytoplasma emulsified in oil is found in the middle layer. This latter is used as the hydrolysing agent.

Hoyer [5] also endeavoured to isolate the ferment, or at least to obtain preparations richer in active substance than the castor seeds themselves. *Hoyer* insisted on the necessity of working in an *acid* medium, but *Nicloux* found in the course of his experiments that the best technical results are obtained [6] in a neutral medium (*e.g.* a solution of magnesium and calcium sulphates), and that it is advantageous, especially in the case of oils and fats containing glycerides of lower fatty acids, to remove the free acids by washing with soda.[1] The retarding effect of lower fatty acids was later on confirmed by *Hoyer*,[2] who found that the castor seeds contain an acid-forming, water-soluble ferment, which produces sufficient acid to " activate " the lipolytic ferment (*Nicloux's* lipaseidin), and which seems to consist of a mixture of volatile fatty acids and lactic acid. A series of experiments undertaken by *Hoyer* with a view to isolating the lipolytic enzyme by means of a mixture of petroleum ether and chloroform [3] (1 volume : 2 volumes) led to the preparation of " ferment-oil," consisting of a mixture of castor oil and protoplasma (*Nicloux's* cytoplasma), and forming about 64 per cent of the original castor seed.

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[1] English patent 749, 1912.

[2] Connstein, English patent 22,111, 1902; *Vereinigte chemische Werke, Act.-Ges.*, German patents 145,413, 147,757; French patent 328,101.

[3] Lewkowitsch, "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.*, 1903, 596; *Report on V. Internat. Congress*, Berlin, vol. ii. p. 544.

[4] French patent 335,902, first addition No. 3192; English patents 8233, 1904; 8304, 1904; German patents 188,511, 197,444.

[5] *Berichte*, 1904, 1436; cp. also French patent 350,122, and first edition to French patent 325,902.

[6] French patent 349,213; German patent 191,113; cp. also Nicloux, *Contributions à l'étude de la saponification des corps gras*, Paris, 1906.

As it was evident that the manufacture of this " ferment-oil " could not lead to a technical process, other experiments were made by *Hoyer* with a view to preparing an emulsion of the lipolytic ferment by expressing the seeds after triturating them with water. But as these experiments proved of no avail, *Nicloux's* process of centrifuging was adopted as the best method in the initial stages, and was followed by the preparation of a " ferment-milk " (termed in technical practice " ferment "). The " ferment " is obtained in the following manner :—Decorticated castor seeds are ground up with a large quantity of water in a suitable mill, and the mass is filtered from the suspended solid substances, whereby a white creamy liquor is obtained. If this liquor is allowed to ferment spontaneously, water separates, and there rises to the top a thick creamy emulsion, consisting of 38 per cent of castor oil fatty acids, 58 per cent of water, and 4 per cent of albuminoid substances. The latter constitute the actual lipolytic agent.[4] Finally, it was found that a better " activator " than magnesium or calcium sulphate (see above) is manganese sulphate, the addition of which to the emulsion has also been patented.[5]

(The accelerating action of certain metallic salts was first discovered by *Pottevin*.[6] Other activators claimed recently are amino-acids and acid amides, obtained by allowing albuminoid substances (such as oil cakes deprived of their oil) spontaneously to undergo proteolytic hydrolysis at 40° C.[7] *Lombard* [8] recommends as an activator ethyl acetate, of which 1 part is stated to suffice for 100,000 parts of oil.)

The manufacturing operations are at present carried out in the following manner :—Oil or fat is introduced into a lead-lined vessel having a conical bottom, and provided with a steam-heating coil and a perforated coil for supplying compressed air. With the aid of the air current an emulsion is produced, whilst about 40 per cent water, 5 to 8 per cent of the "ferment," and 0·2 per cent of manganese sulphate is introduced. After intermixture has been effected, the mass is allowed to stand for one or two or more days, according to the required amount of hydrolysis. During the first hours the mixture must be observed carefully, as separation of the emulsified mass may occur. By stirring afresh, the emulsified state can be re-established, when the ferment begins to exert its action. When the desired degree of hydrolysis is reached, the mass is warmed to 80° to 85° C., and 0·3 to 0·45 per cent (reckoned on the fatty material) of a 50 per cent sulphuric acid is introduced, whilst the mass is stirred (by air). The steam is then turned off, and the contents of the vessel are allowed to settle. The mass separates into three layers—(1) an aqueous layer at the bottom, containing glycerin; (2) a clear layer of fatty matter on the top; and (3) between these two a middle layer consisting of an emulsion of albuminoids, glycerin, fatty matter, and water. This middle layer is allowed to accumulate, and by warming and renewed treatment with water a further separation into three layers can be effected, so that the loss incurred by the formation of this middle layer may be reduced to the smallest possible amount. If the mass has been allowed to rest in the emulsified state for twenty-four hours, the fatty matter contains, as a rule, about 80 per cent of free fatty acids. By allowing the ferment to act for twenty-four hours longer, a further 10 per cent of neutral fat may be hydrolysed.

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[1] Nicloux and Urbain, French patent 349,942.

[2] *Zeits. f. physiolog. Chem.*, 1907 (50), 414.

[3] Cp. also first addition No. 3192 to French patent 335,902 ; and D. E. Haley and J. F. Lyman, *Journ. Amer. Chem. Soc.*, 1921, 33, 2664.

[4] Hoyer prepared the ferment in the form of a powder by extracting the adhering oil and removing the water by drying. Its lipolytic power was, however, thereby so seriously reduced as compared with that of the " ferment," that its commercial application could not be considered.

[5] *Vereinigte chem. Werke*, first addition No. 5562 to French patent 328,101 ; German patent 188,429 ; English patent 25,680, 1905.

[6] *Compt. rend.*, 1903 (136), 767.

[7] Urbain, French patent 350,179.

[8] French patent 346,415.

It is very important to ascertain for each individual oil or fat that temperature which is most suitable for it and to maintain this whilst hydrolysis takes place. It is not advisable to allow the temperature to fall below 20° C., and it is best to work at 2° or 3° C. above the melting point of a fat. As the cytoplasma is readily destroyed when heated to 42° C. in contact with water, it is obvious that tallow is not a suitable material to be hydrolysed by this process, and it is difficult to obtain a product containing 75 per cent of free fatty acids from a low melting tallow, whilst high melting tallows are not workable on a large scale. The hydrolysis of tallow can, however, be effected if it be mixed with suitable oils or fats, so as to reduce the melting point of the mixture to below 35° C.

The ferment must be used in as fresh a state as possible. The author observed that after a few days' standing the lipolytic power becomes greatly reduced. This would be readily explained by the fact observed by *Hoyer*, that the "ferment" is much more easily affected (injuriously) by acids than is the original castor seed pulp. According to *Schimanski*[1] the seeds from *Chelidonium majus* and *Linarium purpureum* contain an even more active enzyme than castor seeds. Seeds belonging to the species *Papaveraceae* and *Pinaceae* are also suitable for this purpose (cp. Vol. II.).

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[1] *Chem. Zeit.*, 1911, 1376.

The fatty acids obtained by this process are much lighter in colour than those from the autoclave process. With regard to the soaps from these fatty acids and the glycerin obtained by this process, see below.

In commerce there are now obtainable linseed oil-, soja oil-, cotton seed oil-, maize oil-, whale oil-, rape oil-, arachis oil-, olive oil-, coconut oil-, palm kernel oil-, and other "fatty acids" which are prepared by any one or more of the foregoing three processes. *Diesser*[1] patents the production of insulating materials obtained by heating fatty and rosin acids with cellulose and its derivatives, and vulcanising the mass obtained.

Nearly related to these products are coconut oil- or palm kernel oil- "fatty acids," or mixtures thereof, obtained as by-products in the "vegetable butter" industry (p. 56).

The mixture of neutral oil and soap obtained as a by-product in the preparation of vegetable butters may either be sold as such (soap stock) or the soap may be decomposed by boiling with a mineral acid whereby a mixture of free fatty acids with varying amounts of neutral oil is obtained (acid oil). The examination of the acid oils embraces the determination of the suspended matter insoluble in ether, moisture, ash, and in some cases the amount of neutral fat is also required. Since these products contain large amounts of volatile fatty acids, precautions must be taken in the determination of the moisture to avoid loss. A method due to *E. R. Bolton and C. Revis*[2] is carried out as follows.

A piece of filter paper about 15 inches by $1\frac{1}{4}$ inches is folded in pleats and coiled so as to allow it to be dropped into a stoppered weighing bottle, having straight sides. The filter paper and bottle are kept in a vacuum dessicator for forty-eight hours before weighing. About 1 gram of the oil is dropped on to the filter paper, and after weighing, the whole is dried in a vacuum desiccator at a temperature high enough to ensure the oil being liquid for a further forty-eight hours.

In the examination of the soap stock the amount of total fatty matter is usually all that is required.

This may be determined by the usual methods. When the soap stock has been derived from coconut or palm kernel oils, salt may be added to the acid solution, in order to throw out the water soluble acids as far as possible. The disadvantage of methods like the one proposed by *Bolton and Revis*[2] is that the amount of substance taken (about 2 grms.) is far too small, it being difficult to get so small an amount adequately to represent the bulk.

In the commercial examination of the fatty matter obtained by the three preceding processes, the amount of free fatty acids, neutral fat, and of unsaponifiable matter is determined in the first instance (see Vol. I. Chap. XI.). For the proper valuation for soap-making purposes the amount of unsaponifiable matter and the colour and odour of the sample must be taken into account.

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[1] German patent 223,071.

[2] *Analyst*, 1918, 160.

3. Derivatives of Fatty Acids

Hydroxylated Fatty Acids.—The manufacture of hydroxy fatty acids from oleic acid has been described already (Vol. I. Chap. VIII.). *G. Imbert*[1] patents the preparation of hydroxylated fatty acids by heating chlorinated fatty acids under pressure with alkalis, alkaline carbonates, and alkaline earths.

Hydrogenised Fatty Acids.—These can be prepared by the methods given above for glycerides, p. 119.

Halogenised Fatty Acids.[2]—The glycerides and esters corresponding to these acids have been described above, p. 129. They are almost exclusively used, usually in the form of the calcium or magnesium salts, for therapeutic purposes.

(*a*) *Chlorinated Fatty Acids.*—These are prepared by methods given on p. 129. *Hoffmann-La Roche*[3] patents the production of chloro derivatives of iodised or brominated acids by acting on the dihalogen derivatives of the fatty acids such as stearolic dibromide or diiodide with thionyl chlorides.[4] *Sulzberger*[5] prepares derivatives of chloral by dissolving the amide of palmitic acid, prepared by dropping palmitic chloride into strong ammonia, in chloral, and heating to 100° C.

(*b*) *Brominated Fatty Acids.*—These are prepared by acting on the fatty acids with hydrobromic acid or bromine dissolved in a suitable solvent (cp. p. 129).

(*c*) *Iodised Fatty Acids.*—These are prepared by the action of iodine or iodine monochloride or monobromide on the unsaturated fatty acids. Thus *Erdmann*[6] prepares triiodostearic acid by acting on linolenic acid with three molecules of iodine monobromide.[7] The *Société pour l'Industrie Chimique à Bâle*[8] patents the production of alkyl esters of diiodo fatty acids. The amides of iodised fatty acids are prepared by treating the amides of the unsaturated fatty acids with iodine or hydriodic acid.[9] The discussion of the therapeutical action of the iodised fatty acids on the animal organism falls outside the scope of this work.[10]

Sulphurised Fatty Acids.—These are prepared by the action of sulphur at high temperatures or sulphur chloride at lower temperatures on the fatty acids, or may be prepared by saponifying the sulphurised oils and liberating the fatty acids (cp p. 129). By sulphonating mixtures of unsaturated fatty acids with aldehydes and ketones, substitutes for turkey-red oil are prepared which, it is claimed, are superior to the turkey-red oils prepared as described (p. 207).[1]

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[1] English patents 17,154, 1906; 11,121, 1908; French patents 368,543, 390,497 (cp. also p. 116); United States patent 901,905; German patent 206,305; Imbert and Consortium f. elektrochem. Ind. German patents 208,699; 212,001.

[2] Ges. f. chem. Ind. in Basel, English patent 28,871, 1910; Italian patent 349/155/114,268; French patent 426,793; Hungarian application C. 1921; Belgian patent 230,815; Hoffmann-La Roche, German patent 249,720; German patent application H. 54,857.

[3] German patent 232,459; Swiss patent 55,667.

[4] English patents 14,323, 1906; 2484, 1907; French patent 326,370; German patents 180,087, 202,353 (Bayer and Company); J. D. Riedel, German patent 202,790; C. Bückel, German patent 281,364.

[5] United States patent 1,025,889.

[6] German patent 233,893.

[7] Cp. Soc. Chem. Ind. in Basle, United States patent 988,066; Muehle, German application M. 49,742; Arnaud, Posternak and Hoffmann-La Roche, United States patent 982,656; Hoffmann-La Roche, German patent 261,211; Swiss patents 49,337, 49,524, 49,525; Schuster, *Zeits. österr. Apoth. Ver.*, 1911, 285.

[8] French patent 430,404; English patent 19,350, 1910.

[9] Newton and Farbenfabrik vorm. Bayer und Co., English patent 18,813, 1911; German application F. 31,123.

[10] Cp. Abderhalden and Hirsch, *Zeits. f. physiol. Chem.*, 1911, 38.

Arsenic and Phosphorus Derivatives of Fatty Acids.—These have been prepared and patented by *Heinemann.*[2]

Amides of Fatty Acids.—These products are manufactured by heating the ammonia salts of fatty acids under pressure. Another process of manufacturing them is patented by *Chemische Werke Hansa,*[3] and consists in treating fatty acids with gaseous ammonia under pressure. The water formed in the process is drawn off, together with the excess of ammonia, and is separated in a drying apparatus, so that only dry ammonia enters the autoclave, and no gas is lost in the process.

The application of amido-acids as emulsifiers has been mentioned already (see p. 117). *Muller-Jacobs*[4] recommends stearamide, $C_{17}H_{35}CONH_2$, in conjunction with alum, for sizing paper. He states that on passing the paper through the calenders the melted stearamide imparts a glaze and " feel " to the paper, whilst at the same time waterproofing it. Experiments made with stearanilide (see below), " stearine," stearic anhydride, and stearone do not produce equally good effects.

A mixture of vaseline with 5 per cent of stearic anilide was brought into commerce under the name *Fetronum purissimum Liebreich.*

Stearanilide, as also stearo-derivatives of other aromatic amides, are stated to possess emulsifying properties, and are therefore recommended for the preparation of salves, etc. (see above, p. 117). *Liebreich* prepared these products[5] by heating fatty acids with an equivalent or excess of aniline, naphthylamine, aromatic diamides, or their alkylates to about 200° C. for twelve to twenty hours. The lower the temperature the longer was the time required for the reaction. The latter is represented by the following equation :—

$$R.COOH. + \underset{\text{Naphthylamine.}}{C_{10}H_7NH_2} = R.CO.NH.C_{11}H_7 + H_2O.$$

(Instead of the fatty acids the original fats themselves may be used ; cp. Vol. I. Chap. I.)

The employment of stearanilide in the colour industry has been patented by *Sulzberger.*[6] The manufacture of the santalol ester of stearic acid has been protected by *E. v. Heyden,*[7] that of the bornyl ester by *Weizmann and Clayton Aniline Company,*[8] and the isobornyl ester by *Schindelmeiser*.[1] The oleic acid esters with terpene alcohols like menthol, and with phenols, have been prepared.[2]

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[1] Farbenwerke vorm. Meister, Lucius u. Brüning, English patent 13,790, 1908 ; German patent 226,222.

[2] German patent 257,641.

[3] French patent 375,921 ; cp. also L. Ottoman, English patent 6731, 1907.

[4] *Zeits. f. angew. Chem.*, 1905, 1141 ; cp. also Spiess, *Papier-Zeit.*, 1908, 1487.

[5] English patent 12,957, 1902 ; French patent 322,026 ; German patents 136,274 ; 136,917.

[6] German patent 188,909.

[7] German patent 182,627.

[8] English patents 8266, 1906 ; 10,798, 1906.

The mannitol ester of stearic acid has also been prepared.[3] The production of cellulose esters has been patented.[4]

Salts of Fatty Acids

Ammonium Salts.—The chemistry of the *ammonium* salts of fatty acids has been described already (Vol. I. Chap. I.). These salts are chiefly used in practice for scouring raw wool. *F. Garelli*[5] advocates the use of ammonia for saponifying fats, the ammonium salts being converted into the sodium salts by treatment with sodium chloride. According to *L. Paul*[6] the ammonium salts of colophony can be boiled in aqueous solution without decomposition if a relatively large excess of ammonia is present. A technical application of ammonium soaps, based on the fact that these soaps have higher melting points than the fatty acids themselves, has been claimed by *C. F. Böhringer and Söhne*.[7] The following table gives the data from which the patentees derive the conclusion that these products can be used as a substitute for "stearine" in the candle industry, and for the manufacture of "solidified alcohol":—

Melting Points of Ammonium Salts of Fatty Acids

Fatty Acid.	Ammonium Salt containing Ammonia. Per cent.	Melting Point. °C.
Oleic acid of melting point, 14-20° C. .	2·85	56
,, ,, ,, ,, 14-20 ,, .	3·88	60
,, ,, ,, ,, 14-20 ,, .	4·20	about 75
Elaïdic acid of ,, ,, 33 . ,, .	3·20	70
Stearic acid of ,, ,, 65 . ,, .	3·30	87
Erucic acid of ,, ,, 32 . ,, .	3·60	52

Garelli, Barbe, and de Paoli[8] propose to separate the stearic and palmitic acids from oleic acid by dissolving their aqueous ammonium salts in hot water—treating fractionally with water, whereby the salts of the solid fatty acids decompose first, or by dissolving the mixed ammonium soaps in water, whereby the oleate is dissolved while the palmitate and stearate float on the top.

Sodium and Potassium Salts.—These salts represent the commercial "hard" and "soft" soaps respectively. They will be fully dealt with in the following section, "Soap Manufacture."

Metal Salts.—These salts will be treated of under "Salts of the Alkaline Earths and Heavy Metals."

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[1] German patent 229,190.

[2] Sulzberger, United States patents 969,420, 970,662.

[3] Bloor, *Journ. Biol. Chem.*, 1910, 427.

[4] *Chem. Fabrik v. Heyden*, French patent 423,197.

[5] *Giorn. Chim. Ind. Appl.*, 1921, 3,487.

[6] *Journ. Chem. Soc.*, 1917, 112, 1, 214.

[7] French patent 383,531; English patent 23,796, 1907; German patent 204,708.

[8] German patent 209,537.

III. SOAP MANUFACTURE[1]

As explained in Vol. I. Chapter III., it is most convenient to subdivide the soaps into two large classes, viz. 1. SALTS OF THE ALKALI METALS; WATER SOLUBLE SOAPS. 2. SALTS OF THE ALKALINE EARTHS AND HEAVY METALS; WATER INSOLUBLE SOAPS; METALLIC SOAPS.

Ammonium soaps,[2] which hitherto have not gained great commercial importance (see above), would be classed with the water soluble soaps.

In technical parlance, the term "soap" applies almost exclusively to the first class, and is extended to that mixture of alkali salts of fatty acids and water (and other substances) which is sold in commerce under the name "soap."

(1) SALTS OF THE ALKALI METALS; WATER SOLUBLE SOAPS

Before the combination of fatty acids with alkali metals had become known, various powdered vegetable roots were used for cleansing purposes, such as *Saponaria off. L.*, *Gypsophila Struthium L.*, *Leontice Leontopetalum L.*, and *Sapindus Saponaria L.* Even to-day these natural products find a limited use.

For the historical survey of the soap industry, the original papers by *Goldschmidt*[3] and *Alpers*[4] should be consulted.

According as to whether the base used for the saturation of the fatty acids be soda or potash we differentiate between HARD SOAPS (SODA SOAPS) and SOFT SOAPS (POTASH SOAPS). The former may contain small quantities of potash soaps (as is the case in high-class shaving and other soaps), whilst the latter may also contain some proportion of soda (as is the case in soft soaps made in summer), but it is convenient to found the classification on the quantity of the preponderant base, as, indeed, is done in practice.

The fatty raw material for commercial soaps may be furnished by any oil or fat of vegetable or animal origin. In fact, all the glyceridic materials enumerated in Vol. II. Chapter XIV. may be used for soap-making, as also those materials which are obtained from waste fats (see Vol. III. Chap. XVI.), provided they do not contain excessive amounts of unsaponifiable matter. Thus an enormous variety of soaps can be produced, and, indeed, is produced on a large scale. But not every oil and fat yields a soap fulfilling the demands made on it for household, toilet, and manufacturers' purposes.

The quality of soap obtained from each individual oil and fat is given under the heading, Vol. II.

Broadly speaking, it may be stated that the vegetable drying oils and marine animal oils are, on account of their consistence, best suited for the manufacture of soft soaps. Also some of the semi-drying oils (maize oil, rape oil) lend themselves especially for this purpose. Solid fats are used preponderantly for making hard soaps; in this category fall also the non-drying oils. Semi-drying oils, as typified by cotton seed oil, may be used as stock material in admixture with other suitable material for both soft and hard soaps.

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[1] Cp. Lewkowitsch, "Modern Views on the Constitution of Soap," *Journ. Soc. Chem. Ind.*, 1907, 590; F. M. F. Feldhaus, *Chem. Zeit.*, 1908, 837.

[2] Cp. German patents 43,340; 72,921.

[3] *Handbuch d. Öle u. Fette*, vol. iii. p. 494.

[4] *Journ. Soc. Chem. Ind.*, 1907, p. 597.

Oils and fats containing oxidised oils, such as blown oils, are unsuitable for soap-making as they invariably give a darker colour and lead to loss of soap-making material.

The art of the soap-maker consists in blending the raw material at his disposal in such a manner as to produce that soap which is most suitable for a given purpose. Hence it is essential that the soap-maker study the properties and the behaviour of each kind of soap, so as to derive therefrom rules to guide him in the proper blending of the raw materials. In every properly equipped soap-works this is done by making soap from individual oils and fats and from mixtures thereof in an experimental soap pan of sufficiently large size to yield half a ton or a ton of finished marketable soap. A detailed survey of this subject, beyond the incidental notes given in the following section, lies outside the scope of this work.[1] For some experiments showing that the cleansing action of soap is due more to its power of dissolving grease rather than emulsifying it, the original paper by *S. Pickering*[2] must be consulted.

Rosin is largely used in conjunction with fatty material in the manufacture of both hard and soft soaps. Although it has not the same valuable properties in every respect which the fatty acids possess, and cannot therefore be used in the production of best toilet soaps, shaving soaps, and soap powders, it must be considered a legitimate substitute for fatty matter, inasmuch as the alkali salts of rosin acids exhibit valuable detergent properties. Too large an amount of rosin in the soap, however, is harmful as it causes a decrease in the amount of lather formed when the soap is used.[3]

An apparatus for the production of solid rosin soap has been patented by *Fischer*.[4] Rosin soaps are sometimes prepared by treating the resinous wood with alkaline solutions.[5]

The fatty (and resinous) raw material is, as a rule, supplied to the soap-maker in a sufficient state of purity to be worked up immediately. In some cases, however, it is necessary to interpose a preliminary purification by sedimentation, or even a process of bleaching (cp. Vol. II. Chap. XIII.), or boiling up with dilute acid (cp. " Bone Fat "), etc. The methods applied to each individual case have been detailed fully in Vol. II. Chap. XIV.

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[1] Useful details will be found in the second part of Merklen's work, *Études sur la constitution des savons du commerce dans ses rapports avec la fabrication*, Marseille, 1906.

[2] *Journ. Chem. Soc.*, 1916, 111, 86; *Chem. Soc. Trans.*, 1917, 111, 86. Cp. also S. Shorter, *Journ. Soc. Dyers and Col.*, 1916, 32, 99; R. T. Mees, *Chem. Weekblad*, 1922, 19, 82; H. G. Elledge and J. J. Isherwood, *Journ. Ind. and Eng. Chem.*, 1916, 8, 793; A. L. Narayan and G. Subrahmanyam, *Phil. Mag.*, 1922, 43, 663; V. Lenher and M. Bueli, *Journ. Ind. Eng. Chem.*, 1916, 8, 701; J. W. M'Bain and H. Martin, *Chem. Soc. Trans.*, 1914, 105, 957; V. Lenher and G. Bishop, *Journ. Phys. Chem.*, 1918, 22, 68; M. G. White and J. Marden, *ibid.*, 1920, 24, 617; S. A. Shorter and S. Ellingworth, *Proc. Roy. Soc.*, 1916, A 92, 231; W. F. Cooper and W. H. Nuttall, *Journ. Agric. Sci.*, 1915, 7, 219.

[3] C. H. Herty and C. W. Willard, *Journ. Ind. and Eng. Chem.*, 1914.

[4] English patent 23,698, 1908.

[5] French patent 432,998.

In those soap-works which start with very impure raw material from waste fats (Chap. XVI.) a purification by means of distillation (cp. p. 238) is necessary ; but the distillation of fatty material in soap-works is only rarely resorted to, for obvious reasons.

1. HARD SOAPS—SODA SOAPS

The earliest processes of manufacturing hard soap (described by *Pliny*) consisted in boiling oils and fats with causticised wood ashes, the potassium carbonate contained therein being converted into caustic potash by boiling with lime.[1] The potash soaps so obtained were converted into soda soaps by treating the soap paste repeatedly with common salt. The theory underlying this manufacturing process has been fully explained in Vol. I. Chapter III. This process has not yet completely died out, and is still used on a small scale in those localities where a cheap and plentiful supply of wood ashes is obtainable. The manufacture of soap in those localities is still passing through the stage of evolution from a house industry to a manufacturing process.

Later on the wood ashes were replaced by " soda ashes " obtained by burning sea-weeds (" barilla," " kelp "). The manufacture of sodium carbonate by the *Leblanc* and the ammonia-processes almost completely extinguished the use of barilla and kelp, and the soap-maker was thereby enabled to obtain manufactured soda (soda ash, sodium carbonate), which he causticised himself in the same manner as that employed for wood ashes. Thus the caustic soda required for the saponification of oils and fats was actually manufactured in the soap-works, and is to a very large extent still being produced by the soap manufacturer.

The development of modern chemical industry led to the production of solid caustic soda in alkali works, commenced in England about 1850, so that the soap-maker has at present the choice of either buying caustic soda in the solid form or himself manufacturing caustic soda solution (" caustic lyes ") from soda ash, by causticising sodium carbonate, and subsequently concentrating the dilute caustic soda solution in vacuum evaporators of simple or multiple type, such as are shown in figures Nos. 24-27 (see below).

The following two processes for the production of hard soaps from *oils and fats* on a manufacturing scale are chiefly in use :—(A) soap-making by the cold process, and (B) soap-making by the hot process. Recently a third process has been introduced on a limited scale, viz.

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[1] Cp. William C. Alpers, " History and Uses of Soap in Pharmacy and Medicine," *Journ. Soc. Chem. Ind.*, 1907, 597.

(C) soap-making by double decomposition of lime soaps and sodium carbonate.

Under the head of "hot process" falls also the method of making soap from fatty acids or soap stock fatty acids. *Rosin* may be likened in this respect to soap stock fatty acids, as the bulk of it can be converted into rosin soap by boiling with sodium carbonate, the remainder only requiring caustic soda to complete the conversion of the rosin into soap. For soaps made exclusively from rosin compare below.

(A) SOAP-MAKING BY THE COLD PROCESS

The oils and fats most suitable for the manufacture of soaps by the cold process are those belonging to the coconut oil group (Vol. II. Chap. XIV.), as they possess the property of being converted into soaps on being stirred together with concentrated caustic soda solutions of approximately the specific gravity 1·35. The plant required for this manufacture is of the simplest construction, and merely consists of an iron or wooden frame into which the fat, previously brought to a temperature of about 35° C., is placed; the fat is then stirred, whilst an accurately measured quantity of caustic soda of specific gravity 1·35 is run in. The frame is then covered and allowed to stand, when the mass develops some heat, sufficient to complete the process of saponification within twenty-four hours.

The simplicity of this process naturally led to the market being flooded with "cold" soaps prepared by unskilled operators, so that these soaps contained a considerable excess of caustic soda, or unsaponified fat side by side with free caustic soda. The prejudice which has arisen against this class of soap is, however, unfounded, as it is not difficult, by careful working, to prepare practically neutral soaps. For this purpose the quantity of caustic soda required for saponification must be calculated from the saponification value of the fatty material. The fifth column of the table, p. 320, will furnish useful guidance.

These soaps are not readily "salted out" by brine; hence they can be used for washing with sea-water (*marine soaps*).

The readiness with which the oils of the coco-nut oil group undergo saponification in the cold enables the soap-maker to induce the saponification in the cold of those oils and fats which are not easily saponified by strong caustic alkalis. This is effected by incorporating with coconut oil certain proportions of olive oil, lard, tallow, etc. The greater the proportion of less readily saponifiable (by strong alkalis) oils and fats, the higher must be the initial temperature at which the oils and fats are intermixed with the strong caustic soda lye.

Soaps so prepared naturally contain the whole amount of glycerol that results from the saponification of neutral oils and fats.

Since 100 parts of neutral glycerides yield practically 150 parts of finished soda soap, it is possible to calculate the theoretical composition of a soap made by the "cold process." Thus a soap made from a coconut oil having the saponification value 240, and the mean molecular weight of the mixed fatty acids 200, will have the following composition :—

	Per cent.
Fatty anhydrides	54·50
Combined sodium oxide, Na_2O	8·86
Glycerol, water, and small quantities of inorganic salts (by difference)	36·64
	100·00

Cold soap cannot be conveniently made on a practical scale from fatty acids or soap stock fatty acids, as in consequence of the immediate combination of fatty acid with caustic soda, lumps are formed which occlude the uncombined materials. For this reason fats containing notable amounts of free fatty acids are unsuitable for the manufacture of cold soaps.

The facility with which these soaps can be made on the smallest scale has brought in its train the manufacture of " cold " soap, adulterated by the incorporation of strong solutions of sodium silicate with the mass whilst still warm. Such soaps frequently contain both free caustic soda and unsaponified fat. Native-made soaps in Egypt are made by the cold process from cotton-seed oil. They are usually heavily loaded with inert fillers.

Castor oil simulates the fats belonging to the coconut oil group by being able to form " cold " soaps. The further property of castor oil of imparting translucency to soap has also been made use of in the manufacture of inferior cold soaps, and complete transparency is obtained by the addition of sugar solutions, together with sodium silicate solution. On the Continent large quantities of cheap transparent soaps of this kind are made. They must not be confounded with the high-class transparent soaps described below.

The quantities of soap made by this process are comparatively small ; the bulk of the commercial soaps is made by the " hot process."

(B) Soap-making by the Hot Process

In soap-making by hot processes either natural oils and fats or the fatty acids derived therefrom are used.

a. **Soap-making from Natural Oils and Fats with Caustic Soda**

The process of soap-making by boiling glycerides with caustic soda solutions is used on the most extensive scale, and is practically the only process which yields soaps of uniformly good quality, colour, and hardness, and at the same time the largest amount of glycerin obtainable from the raw material by means of comparatively simple operations.

In this process the oils and fats are introduced into a cylindrical or square iron vessel—soap kettle, soap "copper," soap pan—and churned up by means of steam, when a dilute caustic soda solution is run in, which assists the emulsifying of the fat and induces rapid hydrolysis. The theory of the process has been described in Vol. I. Chap. II., and it need only be pointed out that it is necessary to commence with a dilute solution of caustic soda, as in the case of most oils and fats—with the exception of the oils belonging to the coconut oil group, and of castor oil—a strong solution "cuts" (relargue) the soap-paste much as does salt solution. It has been shown (Vol. I. Chap. II.) that an excess of caustic soda is required to obtain complete saponification. The mass in the soap pan at this stage (empâtage) consists of a mixture of soda salts of the fatty acids with water, in which the glycerol formed in the course of hydrolysis, and the excess of caustic soda are dissolved. In order to convert the soap-paste into commercial soap, it is necessary to separate the soda salts of the fatty acids from the excess of caustic soda and of water by adding salt, whereby the soda soaps are thrown up (relargage). On allowing to stand, two layers are obtained: (1) a lower aqueous layer, containing salt, glycerol, and excess of caustic soda, (2) an upper curdy mass of soap granules, retaining about 30-35 per cent of water. The lower layer is drawn off, and worked up for the recovery of the glycerol contained in it (see "Glycerine Manufacture").

Apparatus for saponifying *in vacuo* or under pressure have been frequently patented, but there is no advantage in them.[1]

The curdy soap granules left in the pan are boiled up with water ("closed"), so as to form a homogeneous paste, which is again boiled with a little caustic soda to ensure complete saponification, and again separated into two layers in the manner described above.

The soap is once more treated in the same manner, to remove impurities which impair its colour; in some cases it is boiled with a somewhat concentrated solution of caustic soda ("strengthening change") and "salted out" again to a "curd." Finally the "curd" is "fitted," *i.e.* brought into the condition of finished soap.

The art of the soap-maker consists in so "fitting" the soap that it contains just the proper amount of water (which may be called the "water of constitution," see below), and is still "open" enough to allow the intermingled heavier aqueous solution, as also the impurities (which consist to a notable extent of iron salts of fatty acids) to settle out. After the mass has been allowed to rest for a few days, there is found at the bottom of the soap pan a small amount of alkaline solution (which has separated out on cooling; see below), above which rests a layer of dark soap, intermixed with salt solution, containing the excess of caustic soda used. The dark colour is chiefly due to metallic soaps. This layer is termed in practice "nigre" (*i.e.* black, a term taken over from the Marseilles soap-makers [2]). Above this rests the bulk of the finished soap, "neat soap." It is covered on the top by a thin layer of solidified soap of a spongy nature, owing to the occlusion of the air, which on rising gradually to the top of the mass during settling became entangled there on cooling.

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[1] Cp. English patent 8674, 1909 (W. A. Grant).

[2] In Marseilles the "nigre" from genuine "settled" soaps is now termed "le gras."

The excess of caustic alkali in the " neat " soap should be very small ; its amount depends on the care used in the manufacturing operations.

Up till a few years ago soap-making was considered an art, the details of which were supposed to depend on valuable secrets in the exclusive possession of the practical soap-boiler. Hence the " fitting " was left to him, and the amount of caustic soda used in the process depended entirely on his judgment. It must, however, be acknowledged that through constant practice, and in consequence of the stringent demands of the public as regards quality of soap, the soap-boiler brought soap-making to a considerable degree of perfection, so that the production of practically neutral soaps has now become very general.

From the explanations given in Vol. I. Chap. III. (" Hydrolysis of Soap ") practical rules can be readily derived as to how the several stages of soap-boiling should be conducted. It is essential to effect saponification with the least excess of caustic soda. With this object in view it is necessary to work with caustic lyes of known strength. Tables containing the percentages of caustic soda, derived from the specific gravities of solutions prepared from pure caustic soda, are given in Tables 67 and 68 of my *Laboratory Companion*, page 109. The following two tables will be found useful in regulating and controlling the consumption of caustic soda in soap-works.

Caustic Soda Solutions required to saponify Fats of Mean Molecular Weight 670 (*Coco Nut Oil, Palm Kernel Oil*) [*Lewkowitsch*]

Weight of Fat in Tons.	Gallons of Solution of Caustic Soda.			
	20° Twaddell = S. G. 1·1.	40° Twaddell = S. G. 1·2.	60° Twaddell = S. G. 1·3.	71° Twaddell = S. G. 1·355.
·05	21·01	9·46	5·72	4·59
·1	42·02	18·92	11·43	9·18
·15	63·03	28·38	17·15	13·76
·2	84·04	37·84	22·86	18·35
·25	105·05	47·30	28·58	22·94
·3	126·06	56·76	34·29	27·53
·35	147·07	66·22	40·01	32·11
·4	168·07	75·68	45·72	36·70
·45	189·08	85·14	51·44	41·29
·5	210·09	94·60	57·15	45·88
·55	231·10	104·06	62·87	50·46
·6	252·11	113·52	68·58	55·05
·65	273·12	122·98	74·30	59·64
·7	294·13	132·44	80·01	64·23
·75	315·14	141·91	85·73	68·81
·8	336·15	151·37	91·44	73·40
·85	357·16	160·83	97·16	77·99
·9	378·17	170·29	102·87	82·58
·95	399·18	179·75	108·59	87·16
1·0	420·19	189·21	114·30	91·75
2·0	840·37	378·41	228·60	183·50
3·0	1260·56	567·62	342·90	275·26
4·0	1680·74	756·83	457·20	367·01
5·0	2100·93	946·04	571·50	458·76
6·0	2521·12	1135·24	685·80	550·51
7·0	2941·30	1324·45	800·10	642·26
8·0	3361·49	1513·66	914·40	734·02
9·0	3781·67	1702·86	1028·70	825·77
10·0	4201·86	1892·07	1143·00	917·52

Caustic Soda Solutions required to saponify Fats of Mean Molecular Weight 860 (*Tallow, Cotton Seed Oil, Olive Oil, etc.*) [*Lewkowitsch*]

Weight of Fat in Tons.	Gallons of Solution of Caustic Soda.			
	20° Twaddell = S. G. 1·1.	40° Twaddell = S. G. 1·2.	60° Twaddell = S. G. 1·3.	71° Twaddell = S. G. 1·355.
·05	16·37	7·37	4·45	3·57
·1	32·74	14·74	8·90	7·15
·15	49·10	22·11	13·36	10·72
·2	65·47	29·48	17·81	14·30
·25	81·84	36·85	22·26	17·87
·3	98·21	44·22	26·71	21·44
·35	114·57	51·59	31·17	25·02
·4	130·94	58·96	35·62	28·59
·45	147·31	66·33	40·07	32·17
·5	163·68	73·70	44·52	35·74
·55	180·04	81·07	48·98	39·31
·6	196·41	88·44	53·43	42·89
·65	212·78	95·81	57·88	46·46
·7	229·15	103·18	62·33	50·04
·75	245·52	110·55	66·79	53·61
·8	261·88	117·92	71·24	57·18
·85	278·25	125·29	75·69	60·76
·9	294·62	132·66	80·14	64·33
·95	310·99	140·03	84·60	67·91
1·0	327·35	147·41	89·05	71·48
2·0	654·71	294·81	178·10	142·96
3·0	982·06	442·22	267·14	214·44
4·0	1309·42	589·62	356·19	285·92
5·0	1636·77	737·03	445·24	357·41
6·0	1964·12	884·43	534·29	428·89
7·0	2291·48	1031·84	623·34	500·37
8·0	2618·83	1179·24	712·38	571·85
9·0	2946·19	1326·65	801·43	643·33
10·0	3273·54	1474·05	890·48	714·81

The finished "neat" soap, whilst still warm, is run into soap crutching (mixing) machines (holding from 12 to 15 cwts. of soap), wherein perfumes and colouring matters are incorporated with the soap (if desired), and thence into soap frames, in which the warm mass is allowed to cool. In the south of Europe the finished soap is run on to a cemented floor divided off by boards into suitable compartments, about 12 to 14 ins. high (French, *mises*). For the best class of household soaps the cemented floor is covered with paper.

The soap in the frames (or *mises*) requires a few days to solidify. The sides of the soap-frames are then removed, and thus a rectangular soap block is left. This block is cut at first into slabs of the required thickness, either by hand or in a slabbing machine shown in Fig. 20.

These slabs are placed in a barring and tabletting machine, such as is shown in Fig. 21.

The slabs are put into the recess on the right-hand side of the machine. By turning the handle they are pushed through a number of wires, so that they emerge on the other side in the form of bars,

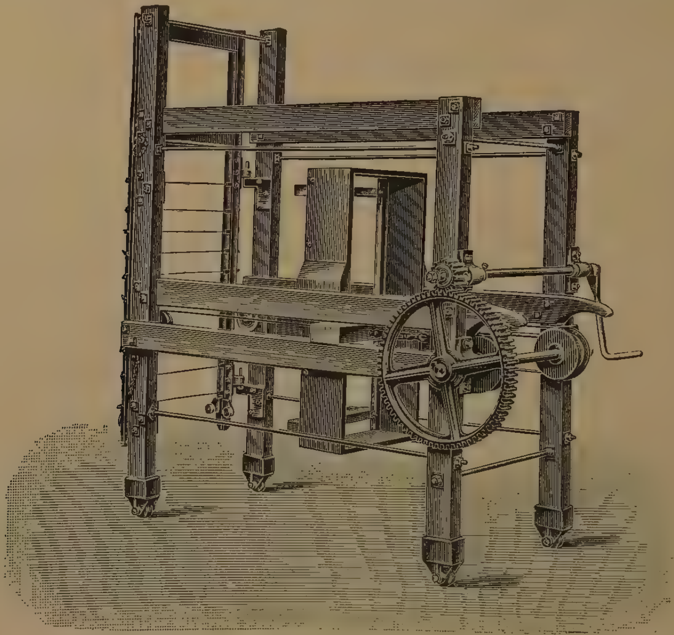

Fig. 20.

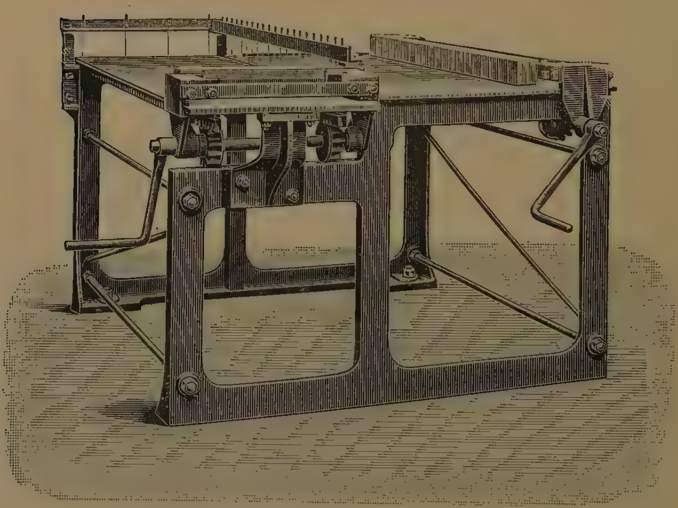

Fig. 21.

usually weighing 3 lbs. By working the handle shown on the left-hand side of Fig. 21 the bars are pushed against the wires shown at the end, and thus finally cut to the desired size and weight of the familiar soap cake. In order to prevent the bars of soap, particularly such soaps as are "heavily run," from adhering together, the surface of the bar is subjected to dry heat in "stoving," applied either in the form of a direct flame or radiant heat or by exposing the soap in a current of hot gas. The thin layer of comparatively dry soap which forms on the surface of the bar, retards, to a large extent, the evaporation of the water from the interior.[1]

The stamping of the soap cakes is a mere mechanical process. For a description of the machines the reader may be referred to the catalogues issued by the makers, and it need only be pointed out that the stamping operations are now done automatically to a very great extent.

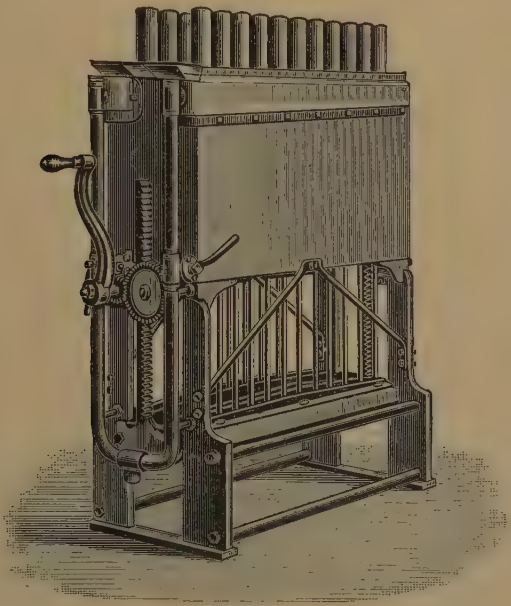

Fig. 22.

The process of solidification of the soap is a somewhat lengthy one. Attempts have therefore not been wanting to shorten the time required from the finishing operation in the soap pan up to the conversion of the solidified soap into the marketable bar or cake.

Cooling machines have been introduced which enjoy, especially on the Continent, a certain vogue. In this country, however, such cooling machines have found but limited use. For the best household soaps the process of cooling in frames has maintained its supremacy. Another attempt to effect rapid solidification of the hot soap mass was made by moulding the hot soap in the same manner as candles are moulded.[1] The machine used for this purpose (Fig. 22) is fashioned after the well-known candle-moulding machines, and was chiefly intended for the manufacture of toilet soaps, in which the crystalline structure, formerly so much valued in household soap, is destroyed (see below). The hot soap mass was run into the row of moulds shown in the figure; after suitable cooling, the solidified soap was expelled in the same manner as moulded candles are forced out of the moulds.

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[1] Higgins and Spensley, English patent 27,889, 1909.

This machine proved unsuitable for household soaps, but the idea underlying its construction has been recently taken up and patented by *Schnetzer*.[2] Another attempt to shorten the time required for solidification has been made by *Klumpp*,[3] whose press is best described as being modelled after a copying press, the sides of which are completely closed. The hot soap is run into the press and when this is full the soap is cooled rapidly and compressed, so that the soap bars are immediately ready for cutting into tablets. Latterly this machine has been made for a somewhat larger throughput than the original apparatus permitted. A combination of the principles embodied in these two methods may be said to be contained in *Schrauth's* patent,[4] which has been followed by a number of further patents [5] by the same inventor.

A very large number of patents [6] have been taken out during the last few years (by many designers) for soap-cooling machines, which embody the principles just described. They embrace a variety of machines having cooling tubes arranged either horizontally or vertically, and working either with or without pressure. A further modification has been introduced by adopting apparatus which entirely simulate filter presses; the chambers of these presses are, of course, provided with cooling arrangements. Although a number of such machines appear to have been installed in small works, too little is known of the results that have attended their working to enable one to arrive at a definite conclusion as to whether the texture and quality of the soap is the same as that obtained by the method of cooling in frames. In the largest soap-works of this country and of the United States these machines have not been adopted hitherto. Even if it should be established that the product obtained by rapid cooling is not inferior (which is doubtful) to soap allowed to cool spontaneously in frames, the high cost of the new apparatus as compared with that of the old system militates against its adoption. Furthermore, the commercial soaps cooled in cooling machines have a tendency to remain soft in the interior. Such soaps sweat to a greater extent than soaps cooled in the ordinary soap frame.

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[1] English patent No. 4581, 1893.

[2] English patent No. 18,932, 1902; German patents 140,505, 144,108, 145,079.

[3] German patents 126,609, 140,846, 211,624.

[4] German patent 144,805.

[5] For cooling frames provided with means for artificial cooling (or even heating as in the case of mottled soaps) cp. S. Baralino fu Gerolamo, German patent 195,581; Boardman, English patent 24,023, 1904; German patent 192,193.

[6] German patents 160,560, 167,306, 167,412, 171,843, 172,691, 178,478, 181,497, 182,854, 186,731 (conjointly with Frankenthaler Kesselschmiede and Maschinenfabrik, Kühnle, Kopp, and Kausch), 198,112; K. E. Markel, English patent 23,187, 1904; Holubek, English patent 24,440, 1904; French patent 347,588; W. Rivoir, English patent 6161, 1905; German patents 170,190, 223,446, 232,504; F. Jürgens, English patent 15,666, 1905; Talvande frères and Douault, French patent 344,006; F. Daum, French patent 345,748; German patent 157,509; Roth, French patent 341,734; English patent 3602, 1905; German patents 172,655, 215,219; A. R. Wilson, English patent 11,622, 1906; Krefelder Seifenfabrik, Stockhausen and Traiser, French patents 357,637, 379,885, 396,945; G. Klinger, French patent 370,086; German patents 204,166, 209,194; Jacobi, English patent 6726, 1907 (in the name of O. Imray); English patent 18,253, 1907; English patents 21,822, 1908; 9590, 1909 (in the name of Bloxam); French patent 386,543; German patents 194,683, 202,710, 208,590, 209,234, 209,270, 211,838, 217,421, 238,490, 260,571; F. H. Merrill, United States patent 831,884; J. Günther, German patents 193,570, 216,528; Weber and Seeländer, German patents 198,865, 201,426; G. Harzer, German patent 201,710, 210,864. Other cooling machines were designed by G. Col, Hauff, German patent 205,473; Leimdörfer, Lehmann, Krull, and by Schou (Eng. pat. 20,916, 1907), 29,048, 1912; Savy, French patent 414,252; F. Schmidt, German patent 227,906; Hampe, German patent 221,494; Rost, German patent 224,665; Moore-Irvine, English patent 14,623, 1908; Gilbert and Ralph, English patent 18,031, 1908; Morel, French patent 446,898; Schüssler and Derscherl, Austrian patent 49,059, 1910; Bontoux, *Chem. Zeit.*, 1911, 94; J. Leimdörfer, German patent 273,719.

In this connection it may be pointed out that *Cressonnières frères* constructed, some twenty-five years ago, a continuous drying machine,[1] which took the finished soap, in the hot state, from the soap pan on a long travelling band, and dried it, in a hot room, to such an extent that it had lost sufficient moisture to permit of it being worked up into cakes in the plant usually employed for making best toilet soap (see below). This drying machine was also recommended for the manufacture of household soap, but as the working conditions of the toilet soap plant proper required that the " genuine " soap must lose so much moisture that the finished product contained about 75 per cent of fatty acids—against 63-64 per cent in the ordinary household soap—it has been impossible to introduce this apparatus into soap-works with a view to replacing the ordinary cooling frame.

100 parts of neutral glycerides of the mean molecular weight 860 yield on a practical scale 150 parts of genuine soap. The mean molecular weight of the fatty acids of such glycerides is 275. An easy calculation will show that 100 parts of fat require 10·77 parts of Na_2O = 13·03 parts of NaOH ; hence the finished soap contains 7·18 per cent of Na_2O [$150 : 10{\cdot}77 :: 100 : x$], with which are combined 61·6 per cent of fatty anhydrides [$31 : 266 :: 7{\cdot}18 : y$], corresponding to 63·7 per cent of fatty acids [$266 : 275 :: 61{\cdot}6 : z$].

The percentage composition of a " genuine soap " is therefore—

	Per cent.
Fatty anhydrides	61·60
Combined sodium oxide, Na_2O	7·18
Water, including small quantities of inorganic salts and glycerol (by difference)	31·22
	100·00

Pure commercial soda soaps made by the processes described contain practically 30 per cent of water and 63 to 64 per cent of fatty acids.

Thus *Okada*[2] found for a freshly prepared commercial soap the following figures :—

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[1] Cp. also G. L. Baker, English patent 15,264, 1907 ; Boardman, English patent 2266, 1910 ; Klumpp, German patent 258,440.

[2] *Chem. Zeit.*. 1911, 230.

	Per cent.
Fatty acids	62·7
Combined alkali, Na_2O	7·2
Free alkali, Na_2O	0·6
Water	28·5

which, calculated on the dry substance, corresponded to

	Per cent.
Fatty acids	87·7
Combined alkali, Na_2O	10·1
Free alkali, Na_2O	0·8

The commercial soaps were, therefore, looked upon as a kind of crystalline compound, containing a definite amount of water which was considered "water of crystallisation." Some slender support to this view was lent by the fact that in soaps containing the above-named proportion of fatty acids, a kind of crystallisation ("feather") was noticeable; this crystallisation was considered to be due to the harder stearates and palmitates separating out in a semi-crystalline form from the magma of oleate.

In the course of a long series of experiments which the author carried out on a large scale on many tons of varied fatty materials, with the object of producing a commercial soap having a higher proportion of fatty acids than 63 to 64 per cent, he was never able to obtain a soap of the desired higher percentage. Hence the author adopted the view that this proportion of water might be termed "water of constitution," inasmuch as a commercial soap having less water cannot be made in the soap kettle.

This explanation has been attacked by *Merklen*,[1] whose fundamental view, based on the application of the laws of chemical equilibrium and of the phase rule to the present problem, is as follows: Commercial (genuine) soap is not a product which has a definite composition, but has, on the contrary, an essentially variable composition. The actual composition of a given commercial (genuine) soap depends (1) on the nature of the fatty acids, (2) on the composition of the "nigre" (in the case of "settled" soaps), and (3) on the temperature at which the boiling is conducted. Another important factor conditioning the ultimate composition would be the pressure; but since soap is always made at the ordinary pressure, this factor, representing, as it were, a constant, may be left out of consideration.[2] The finished soap behaves like a colloid.[3] Commercial soap should, therefore, in *Merklen's* opinion, be looked upon as an "absorption-product,"[4] the most characteristic property of which is its continuous variation. The absorption of water by the colloid soap being a function of (1) the nature and structure of the colloid; (2) the nature of the solvent; (3) the nature of the salts and the alkali ("electrolytes"); and (4) the temperature, the variations in the composition of the commercial soap would be explained by variations in the factors set out above. Briefly stated, soap should not be looked upon as a compound of sodium salts of fatty acids with which a definite amount of water is combined chemically, but rather as an "absorption-product," the composition of which is a function of the environment in which the sodium salts of the fatty acids happen to be found at the moment of the finishing operation.

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[1] *Études sur la constitution des savons du commerce dans ses rapports avec la fabrication*, Marseille, 1906.

[2] It may be mentioned here that patents have been taken out for the production of soap under pressure as also in a vacuum.

[3] The view that soap behaves like a colloid was adopted, and fully developed, by Krafft and Wiglow, *Berichte*, 1895, 2573. With regard to the objections of Kahlenberg and Schreiner to Krafft's theory and the rejoinder of the latter, see Lewkowitsch, *Jahrbuch d. Chem.*, 1899, ix. 352; cp. also Vol. I. Chap. III.

[4] In more modern parlance the term "ad-sorption product" would be used. The theory of ab (ad) sorption products has been developed by van Bemmelen (*Landw. Versuchsanst.*, 1878 (31), 135; (33), 265; 1888 (35), 69; *Journ. f. prakt. Chem.*, 1880 (23), 324; 379; *Zeits. f. angew. Chem.*, 1900 (23), 111; 123.

It should be pointed out that the process of saponification itself has nothing to do with these views, it being immaterial whether the soap-paste obtained in the first operation be produced from neutral fats and caustic soda, or from fatty acids and sodium carbonate. Such difference as does exist does not affect the principle of the present question, but only such minor points as absence or presence of glycerol, difference in the composition of the aqueous solution, etc

In the light of these views, the practical operations involved in the production of a "settled" soap in the soap pan may be explained as follows:—The soap-paste, which may, or may not, contain an excess of alkali, is treated with common salt. The latter absorbs and withdraws water from the pasty mass, and when a certain concentration of the salt solution is reached, the soap is thrown up in a curdy form, poor in water and rich in salt. These curdy soap granules occlude some of the saline solution. The more concentrated is the salt solution the less water is retained by the soap granules, or "curd." The composition of the "curd" is at this stage a function of the composition of the salt solution, which may contain free caustic alkali, sodium carbonate, and also glycerol, etc., as the case may be. After withdrawing the lye, and preparatory to boiling with the "strengthening" change, water (and a small quantity of caustic alkali) is added to "close" the soap. The grains of soap absorb water, parting with salt until the salt solution has become so dilute that it dissolves soap, and finally a homogeneous mass is obtained. The next operation is merely a repetition of the process of graining, with this difference, however, that the salt solution is now made less concentrated than before, with a view to producing a less coarse grain, so as to facilitate the operation of "fitting" (see above). The mass in the soap pan represents at this stage a biphasic system, the two component phases of which have been characterised already. The composition of the two phases differs, whilst their constitution is the same; both contain the same substances, only in different proportions; both are colloidal solutions of sodium salts of fatty acids in an alkaline salt solution, only the proportions of salts and soap varying to a considerable extent (see below).[1]

On cooling we should, therefore, obtain two layers only, viz. "neat" soap and “nigre.” As stated above, frequently three layers are found, the third layer being a strong salt solution below the nigre. The occurrence of this third layer is readily explained. At the temperature of the finishing operation the nigre is essentially an alkaline salt solution, holding so much soap in solution as corresponds to the then prevailing temperature. If the “nigre” cools, the equilibrium can no longer remain undisturbed, and a portion of the saline solution separates out, leaving the nigre richer in soap than it was at the highest temperature reached during the boiling operation. (If the soap pan is well protected against loss of heat by radiation, it may happen that no salt solution separates, *Lewkowitsch.*) From the large numbers of experiments published by *Merklen* in support of his views, one example may be given as typifying the boiling of a tallow soap.

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[1] M. E. Laing and J. W. M'Bain, *Chem. Soc. Trans.*, 1920 (117), 1506; W. Darke, J. W. M'Bain, and C. Salmon, *Proc. Roy. Soc.*, 1921 (A 98), 395; J. W. M'Bain and H. E. Martin, *Chem. Soc. Trans.*, 1921 (119), 1369; J. W. M'Bain and C. S. Salmon, *ibid.*, 1921 (119), 1374.

The “neat” soap gave the following numbers :—

		Per cent.
Water		36·10
Fatty anhydrides	56·77	
Combined alkali, as Na_2O	6·59	
Anhydrous soap	———	63·36
Free alkali		0·25
Sodium chloride		0·29

It should be pointed out that the amount of “anhydrous soap” is too low for a “genuine” commercial tallow soap.

The “nigre” consisted of three layers :—

(1) The uppermost layer, yielding the following numbers—water, 36·40 per cent; free alkali, 0·28 per cent; sodium chloride, 0·29 per cent; anhydrous soap (by difference), 63·03 per cent—has approximately the same composition as the “neat” soap.

(2) The next layer, forming the middle portion of the “nigre,” gave the following numbers :—Water, 53·40 per cent; free alkali, 0·73 per cent; sodium chloride, 0·90 per cent; anhydrous soap (by difference), 44·97 per cent.

(3) The lowest layer, forming the well-known greyish spongy mass, furnished the following numbers on analysis :—Water, 68·30 per cent; free alkali, 1·31 per cent; sodium chloride, 1·85 per cent; anhydrous soap (by difference), 28·54 per cent.

The “lye” below the “nigre” contained :—Sodium carbonate, 0·86 per cent; sodium hydroxide, 1·87 per cent; sodium chloride, 3·40 per cent. The composition of the nigre is thus obviously a function of the temperature; the composition changes continually with the fall of the temperature, and the change is only arrested when the mass solidifies.

Views similar to those developed by *Merklen* have been published, at the same time and independently of *Merklen*, by *Leimdörfer*.[1]

The fact that all genuine commercial soaps boiled on a “nigre” contain approximately the same percentage of fatty acids (the variations amounting to no more than 1 per cent if proper care be exercised) may be explained in the light of *Merklen's* views by the fact that in the process of manufacturing these soaps (termed "settled" soap as they are allowed to "settle" on a nigre) the soap-maker chooses as constants not only the temperature and the pressure, but also the proportion of free alkali in the "nigre" and the amount of soap held in solution by the nigre. The last two conditions implicitly postulate that the amount of salt must also be approximately constant. (Indeed, a number of well-made household soaps examined by *Lewkowitsch* contained less than 0·5 per cent of sodium chloride and less than 0·1 per cent of sodium sulphate.) Such slight variations as actually do occur may then be ascribed to slight variations in the composition of the nigre, the amount of salt left in the neat soap, etc. It may, indeed, be granted that these factors are fairly constant in practice, as in the large modern soap-works all working details are so carefully observed that soaps having practically identical compositions are manufactured from week to week without any difficulty whatever. In practice those oils and fats, which if used alone do not yield a "settled" soap of 63 per cent of fatty acids, are mixed with other oils and fats, so that the mixture yields a "settled" soap of 63 to 64 per cent of fatty acids.

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[1] *Seifensieder Zeit.*, 1906, Nos. 24 to 29; *ibid.*, 1910, Nos. 28 to 43.

If it be accepted as a fact that the percentage of 63 to 64 per cent of fatty acids is the maximum obtainable in a "settled" soap, it would appear immaterial whether the water (or, to speak more correctly, the dilute salt solution) which a "settled" soap retains be considered as the maximum amount of water (or solution) which the colloid—sodium salts of mixed fatty acids—can absorb, or whether it be looked upon as "water of constitution." If, however, it were possible to prepare a commercial "settled" soap containing more than 63 per cent of fatty acids, *i.e.* more than 69 per cent of anhydrous soap, then the theory which assumes "water of constitution" must fall to the ground, and the explanation that soap is a colloid would certainly deserve preference.

Amongst the analyses *Merklen* published in detail there are many which lead to less than 69 per cent of anhydrous soap, and hence do not represent "genuine" soaps; but there are six which lead to 71-74 per cent of anhydrous soap. This appears to the author to be inconsistent with his own very extensive experience.

The author's difficulty might be met by the contention that the "settled" soaps found in commerce contain too much water in their freshly prepared state, and that they would part with more water (*i.e.* dilute salt solution) on settling in the soap pan, if they did not solidify too soon. And it might further be urged in view of the author's difficulty that the colloid which absorbs the maximum of water and the minimum of salt is that one which is obtained in the process of "graining" with the most concentrated salt solution. Of course such grained soap occludes, mechanically, portions of that concentrated salt solution, and would therefore show a much lower percentage of fatty acids than 63 to 64 per cent. Experiments were therefore undertaken by the author[1] in which the grained soap was subjected to pressure in order to remove the occluded salt solution, the amount of salt used in the three succeeding experiments being gradually reduced to the smallest amount possible.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1907, 590.

Pure tallow was converted on a practical scale into a genuine commercial soap. This finished soap contained anhydrous soap, 67·00 per cent; sodium chloride, 0·934 per cent. This soap was boiled up with water to a homogeneous paste and treated with solid salt, until an excess of salt was found at the bottom of the salt solution. The curdy mass was expressed, first by hand in a cloth, then in a spindle press up to a pressure of 20 lb., then at 40 lb., and finally in a hydraulic press at a pressure of 75 atmospheres. The percentages of fatty acids in the successively prepared "soaps" were as follows:—38·0 per cent, 58·6 per cent, 62·8 per cent, and 65·4 per cent. The edges of the press cake were then cut off and removed, the remaining mass was roughly broken, and pressed again at a pressure of 100 atmospheres. The resulting soap contained—anhydrous soap, 73·10 per cent; sodium chloride, 22·18 per cent. The mass was, of course, not a commercial soap, being merely a mechanical mixture of 22·18 per cent of sodium chloride, 73·10 per cent of anhydrous soap, and 4·72 per cent of water.

Evidently in this experiment too much salt had been used in the "graining." Hence in the following experiment the "graining" was performed by careful addition of a saturated brine solution to the soap jelly (prepared as above) until a clear separation of the "curd" had taken place. The curd so obtained was pressed as before. The mass pressed at a pressure of 75 atmospheres contained 68·4 per cent of fatty acids. Subjected to a pressure of 100 atmospheres it yielded 69·6 per cent of fatty acids. Finally, after pressing at 150 atmospheres, the mass contained:—Anhydrous soap, 85·24 per cent; sodium chloride, 1·74 per cent; water (by difference), 13·02 per cent. This mass differed, of course, very much from a commercial soap.

As the proportion of salt must still be considered too high, the commercial genuine soap which formed the starting material was shredded and pressed up to 150 atmospheres. The expressed mass contained:—Anhydrous soap, 73·88 per cent; sodium chloride, 0·87 per cent; water (by difference), 25·25 per cent. This mass was, however, not a commercial soap, but rather that form of soap which is ready for the plodding machine in the manufacture of a toilet soap (see below).

The foregoing experiments have not removed the difficulty which the author finds in fully accepting *Merklen's* views, and it is impossible to reconcile the latter's statement, viz. that he obtained those six commercial soaps with more than 69 per cent of anhydrous soap, with the author's own experience.

Although *Merklen* adds, in a footnote to the German edition of his work,[1] that he obtained a commercial palm oil soap containing even 77 per cent of fatty acids, the author has not the slightest hesitation in stating that this result is absolutely incompatible with the composition of a commercial soap made in the soap kettle.

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[1] Translated by F. Goldschmidt, Halle a/S., 1907, p. 77.

When a concentrated solution of soap is dialysed the solution becomes milky, due to the free alkali formed by hydrolysis of the soap diffusing out and leaving behind the fatty acids and acid soaps.[1]

A serious objection to the view that commercial genuine soap is a colloid may further be found in the fact that sodium and even potassium stearate (or palmitate) crystallise out in commercial soap; this can be well observed in a soft soap, on account of its transparency. This crystallisation can be produced at will ("figging," see below), and is obtained by admixing some tallow with linseed oil in making soft soap. In course of time the crystals grow and permeate the whole mass of soap. This is all the more noteworthy as, viewed in the light of the foregoing explanations, a commercial soft soap must be considered as a much better representative of a colloidal solution of soap than commercial hard soap, which contains less water. In the hard soap the formation of a crystal (indications of which are shown by the "feather" in soaps containing large amounts of hard fats) would appear to be prevented by the rapid solidification of the soap mass, much as in the case of solid fats the crystallisation of "stearine" in the magma of "oleine" is prevented by somewhat rapid cooling (whereby the whole mass solidifies to a homogeneous body, cp. Vol. II. Chap. XIII.).

From a study of the physico-chemical properties of soft soap (viscosity and electrical conductivity) *Goldschmidt and Weissmann*[2] support the view that soap behaves like a colloid.

A confirmation of the author's view, and inferentially a further objection to the generalisation of *Merklen's* view, may be found in some observations made recently by *W. D. Richardson*[3] in the examination of ordinary commercial soaps under the polarising microscope, when indications of crystalline structure were noticed.

Richardson points especially to the formation, in transparent hard soap (see below), of crystals which become noticeable from four to eight weeks after the soap has been finished. These crystals were observed to grow in size and number for an indefinite time. (This would point to a similarity between these crystals and those appearing in a "figged" soft soap; cp. above.)

After separating (by hand) the crystals from the non-crystalline magma, it was found that the composition of the crystals was that of ordinary pure soap, and that the fatty acids melted at 43° to 44° C., whereas similarly prepared fatty acids from the still transparent portion of the soap melted from 36° to 38° C. The crystals can be made to grow artificially, by introducing them into a cake of transparent soap (of such a composition that crystallisation is not made altogether impossible as by the presence of a large amount of such substances as alcohol or sugar solution).

In some experiments, holes were made with a cork borer in bars of transparent soap, which contained no crystals, and into these holes plugs of soap cut from a crystalline bar with the same cork borer were pressed. Around the plugs so introduced masses of crystals formed and proceeded to grow.

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[1] Botazzi and Victoroff, *Atti R. Accad. Lincei*, 1910, v. 659.

[2] *Zeits. Electrochem.*, 1912 (18), 380; cp. also M'Bain, James and Taylor, *Zeits. f. phys. Chem.*, 1911, 179; and A. M. King, *Journ. Soc. Chem. Ind.*, 1922, 147 T.

[3] *Journ. Amer. Chem. Soc.*, 1908, 414. A gradual transition from true solutions to colloidal "sols" and finally to colloidal "gels" can be observed experimentally in the case of a cerohydroxide in glycerol (cp. Vol. I. Chap. III. p. 192).

In other experiments, crystals were ground in a mortar and introduced into transparent soap just about to solidify, when the soap eventually became converted into a mass of crystals. It remains doubtful whether these crystallisations are caused by nuclei of soap crystals, for no crystals were formed if an alcoholic solution of " soap crystals " was added to a non-solidified transparent soap, which had been filtered in order to remove any solid substances present. (Further experiments must show whether nuclei of soap crystals are required to start their formation or growth, for hitherto it has only been shown that particles of crystalline silica, although left in transparent soap for one and a half years, did not induce formation of crystals, even though a soap of identical composition gave a large crop of crystals when " seeded " with soap crystals.)

In the manufacture of genuine settled soaps the tendency to form crystals is purposely destroyed. By passing the soap, whilst still in its hot and glassy transparent state, through the mixing machine, the process of cooling is even accelerated, so that solidification sets in all the more rapidly.

In order to ascertain whether a gradual " crystallisation " (or a kind of " segregation " of " crystalline " or " semi-crystalline " salts) would take place if drying out were prevented in a genuine (household) soap containing considerable proportions of tallow fatty acids, the author had a number of soap tablets wrapped in several layers of tinfoil and grease-proof paper immediately after they had been cut out from a soap block, and had been stamped. They were kept for one year side by side with samples from the same block of soap wrapped in the ordinary manner, so that drying out could take place.

After this lapse of time the samples were unwrapped. Those in tinfoil, etc., had completely retained their weight and showed on freshly cut surfaces most distinctly a crystalline appearance (" feather "), more distinctly even than is observed in those tallow-rosin soaps in the manufacture of which the appearance of " feather " is aimed at. The check samples had dried out to a considerable extent, but the innermost portions of the soap, which were to some extent protected from drying, showed no sign of a crystalline appearance.

Richardson is of the opinion that, amongst other influences and conditions affecting the formation of crystals, desiccation is necessary to bring about conditions suitable for crystal formation, and states that as desiccation proceeds there is apparently produced in the soaps an increase in strain, as is shown by the transmission of light between crossed Nicols. *Richardson's* conclusions refer to transparent hard soap. (Unfortunately, he does not state whether the transparent soaps were " filled " soaps or not.)

The foregoing observations on genuine household soaps (containing approximately 30 per cent of water) would, however, show that desiccation has, on the contrary, an inhibiting influence. This is further confirmed by the well-known fact that " figging " in a soft soap takes place throughout the whole mass in closed vessels when no evaporation can take place.

The weight of experimental evidence would thus far appear to be greater on the side of the supporters of the view that genuine hard soaps, containing 30 per cent of water, are, or at least contain, crystalline bodies, the crystallisation (or partial crystallisation) of which is so easily prevented that they simulate colloidal solutions. Most certainly such soaps are converted into solutions behaving like colloidal solutions if a larger proportion than 30 per cent of water be admixed with the sodium salts. The chemical composition of the fatty acids plays, however, an important part, and generalisations must not be carried too far, as obviously the fatty acids from tallow (which is rich in stearic acid) must behave differently from those of olive oil (which contains practically no stearic acid). The same argument must hold good, to some extent, of potash soaps ; those made exclusively from linseed oil exhibit no tendency to crystallisation, which is, however, readily engendered by a small proportion of stearate introduced as tallow.

Much of the apparent conflict between the views held by *Merklen* on the one hand, and by the author on the other, may disappear when more detailed account is taken of the compositions of commercial soaps, both as regards the nature of the fatty acids and the proportion of water. This problem must therefore be attacked on the basis of experiments, which alone will lead to a decision, and it need therefore only be pointed out that no sharp distinction can be made between crystalloids and colloids, but that there is a continuous transition without a break between true and colloidal solutions.[1]

β. Soap-making from Fatty Acids (" Soap Stock Fatty Acids ")

It is evident, as soap consists essentially of sodium salts of fatty acids, that soap may also be made by neutralising fatty acids with caustic soda, followed by working and " fitting " the resulting mass in the manner described above, p. 318. This process of soap-making was first suggested by *Chevreul*, and has, indeed, been in practical use ever since the stearine candle industry was established, the manufacture of soap from oleic acid affording a natural outlet for this by-product. Since fatty acids are capable of expelling carbonic acid from sodium carbonate when boiled in aqueous solution, soap can also be made by boiling fatty acids with sodium carbonate.[2]

The oleic acid used for the manufacture of oleine soap with caustic soda or sodium carbonate is, as a rule, " saponification oleine " containing varying amounts of stearic and palmitic acids, which give the soap a much harder consistence than that possessed by soap made from an oleic acid which is practically free from solid acids.

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[1] J. Kurzmann, *Kolloidchem. Beihefte*, 1914 (5), 427 ; F. C. Beedle and T. R. Bolam, *Journ. Soc. Chem. Ind.*, 1921, 27 T ; J. M'Bain, *ibid.*, 1918, 249 T ; C. S. Salmon, *Chem. Soc. Trans.*, 1920 (117), 530 ; M. Fischer, *Journ. Soc. Chem. Ind.*, 1922, 139 R.

[2] Irving, English patent 6304, 1908.

The initial manufacturing operation is practically tantamount to neutralising the fatty acids with caustic soda or with sodium carbonate, as the case may be. The precaution must, however, be taken that first the aqueous solution of caustic soda or sodium carbonate is put into the soap pan, and that the oleic acid is allowed to run in slowly whilst the mass is kept boiling, in order to avoid the formation of lumps of soap. If sodium carbonate be used, the boiling must be conducted with great circumspection, so as to facilitate the evolution of carbonic acid and to prevent the boiling over of the fobbing mass.

Oleine soap is chiefly made in candle-works. Notwithstanding the fact that sodium carbonate is cheaper than caustic soda, many candle-makers still adhere to the boiling with caustic soda (to the exclusion of sodium carbonate), as the higher cost of the caustic alkali is more than counterbalanced by the ease of working with caustic soda and the avoidance of losses which are apt to occur through boiling over when sodium carbonate is employed (cp. below).

Oleic acid soap is largely used in the textile industry, especially for scouring silk goods. The great solubility of the oleine soap in water is no doubt the cause of preference being given to this soap over soaps made from other fatty material. It is impossible to prepare a soap by the cold process exclusively from fatty acids.

In consequence of the establishment of special "deglycerinising" works (see above) the manufacture of soap from "soap stock fatty acids" has gained some extension, especially in small soap-works on the Continent, one of the chief advantages claimed for these raw materials being the saving in cost afforded by using sodium carbonate in place of caustic soda, of course, as far as the proportion of free fatty acids permits.

The amount of sodium carbonate required is calculated from the acid value of the sample. The following table, giving the amounts of pure sodium carbonate, Na_2CO_3, and of soda crystals, $Na_2CO_3 + 10H_2O$, required for the acid values set out in the first column, will be found useful in practice. It should be added that the quantities must be slightly increased in proportion to the impurities in commercial soda and commercial soda crystals :—

[Table

Sodium Carbonate, or Soda Crystals, required to neutralise the Free Fatty Acids in "Soap Stock Fatty Acids" (Lewkowitsch)

	Sodium Carbonate, CO_3Na_2.		Soda Crystals, $Na_2CO_3+10H_2O$.	
Acid Value.	Kilograms per Ton of Fatty Material.	Lbs. per Cwt. of Fatty Material.	Kilograms per Ton of Fatty Material.	Lbs. per Cwt. of Fatty Material.
1	0·95	0·106	2·55	0·285
2	1·89	0·212	5·1	0·571
3	2·84	0·318	7·65	0·867
4	3·79	0·424	10·20	1·14
5	4·73	0·530	12·75	1·43
6	5·67	0·636	15·29	1·71
7	6·61	0·742	17·84	2·00
8	7·55	0·848	20·39	2·28
9	8·50	0·954	22·94	2·57
10	9·45	1·06	25·49	2·85
11	10·39	1·16	28·05	3·14
12	11·34	1·27	30·59	3·43
13	12·28	1·38	33·14	3·71
14	13·23	1·48	35·69	4·00
15	14·17	1·59	38·24	4·28
16	15·11	1·70	40·78	4·57
17	16·06	1·80	43·33	4·85
18	17·01	1·91	45·88	5·14
19	17·95	2·01	48·43	5·42
20	18·90	2·12	50·98	5·71
21	19·84	2·23	53·53	6·00
22	20·79	2·33	56·08	6·28
23	21·73	2·44	58·63	6·57
24	22·68	2·54	61·18	6·85
25	23·62	2·65	63·72	7·14
26	24·57	2·76	66·27	7·42
27	25·51	2·86	68·82	7·71
28	26·45	2·97	71·37	8·00
29	27·40	3·07	73·92	8·28
30	28·34	3·18	76·47	8·56
40	37·80	4·24	101·96	11·42
50	47·25	5·30	127·45	14·27
60	56·68	6·36	152·94	17·12
70	66·13	7·42	178·43	19·97
80	75·60	8·48	203·92	22·82
90	85·02	9·54	229·41	25·68

From the difference between the acid and saponification values the amount of neutral fat in the soap stock fatty acids is calculated. This neutral fat, which cannot, of course, be saponified by means of sodium carbonate, must be finally saponified by the addition of caustic soda. The quantity of caustic soda solution required is found in the tables given above.

In small works the sodium carbonate (or soda crystals) required is best weighed out and then dissolved in the soap pan in a suitable amount of water, for sodium carbonate solutions of higher concentration than about 14 per cent of carbonate cannot exist at 15° C.,[1] and more concentrated solutions prepared in the hot will crystallise out if the temperature falls, thus causing great inconvenience in a works. It is of course possible, by a suitable arrangement of tanks and heating coils, to keep a stock of sodium carbonate solutions of much higher concentration.

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[1] A table giving the percentage of sodium carbonate in solutions from 1° Twaddell to 30° Twaddell will be found in the author's *Laboratory Companion to Fats and Oils Industries*, p. 118.

The neutralisation of the soap stock fatty acids is carried out in the same manner as is described under the manufacture of oleine soap. The soda solution must be heated first in the soap pan, and the soap stock fatty acids introduced in small quantities, care being taken not to run in a further quantity before the carbonic acid has escaped so far that frothing over is not likely to take place. It follows, of course, that the soap pan must be of much greater capacity than is required in the case of the same amount of soap made by the process described under (*a*), as ample space must be allowed for the tendency of the effervescing mass to rise rapidly. It is of the utmost necessity to keep the mass well boiling. Some operators even pass a current of air[1] through the boiling mass in order to facilitate the escape of the carbonic acid. This contrivance cannot, however, be recommended.

When all the carbonic acid has practically escaped, the amount of caustic soda required for the saponification of the neutral fat is introduced; the boiling is then continued, and the soap further treated in exactly the same manner as described above (p. 318).

Having regard to the exaggerated statements that are made by interested parties as to the advantages resulting to the soap-maker by working with soap stock fatty acids instead of with natural oils and fats, the fact should be emphasised that soaps of best quality are obtained only by boiling glycerides with caustic soda, as described under (*a*). If "soap stock fatty acids" are actually prepared in the soap-works, an unnecessary complication and a series of cumbersome processes are introduced which do not belong to a soap-works proper. But even at best these processes have several very serious drawbacks as compared with the natural process of the soap-maker described above. The saving brought about by the lower cost of sodium carbonate, as against the equivalent amount of caustic alkali, is more than counterbalanced by the increased expense for larger plant, for more steam (required to heat up the more dilute solutions), for the possible occasional losses (through boiling over), and for the losses of carbonate and of salt in the spent lyes (from which the carbonate and the salt cannot be recovered at a remunerative expenditure). In this connection, it may be mentioned that, in the endeavour to bring this method more into vogue, patents[2] have been taken out for the recovery of carbonic acid, evolved on making soap from soap stock fatty acids, and that in another patent[3] claim is made for the production of soda (by the ammonia soda process) from the carbonic acid evolved in the soap pan. In order to increase the yield of carbonic acid, it is even suggested in the patent specification to neutralise the soap stock fatty acids with sodium bicarbonate in place of carbonate. It is obvious that these processes have never been worked on a practical scale. It must further be pointed out that the glycerin formed from the neutral fat in the soap stock fatty acids (from 1·5 to 2 per cent of the total charge) is lost, for the soap lyes obtained in the process under consideration contain so small a percentage of glycerin that it does not pay to recover it; whereas in the process of boiling, described under (*a*), the full amount, as far as is practicable, is recovered. The fact that what glycerin is recovered by making soap stock fatty acids is more valuable because containing less salt must be admitted, but the loss of actual glycerin far outweighs the supposed gain. Over and above this, it has been proved by extensive practical experience that soaps prepared from such material are of a lower grade as regards colour, and have a notably softer consistence than have the soaps made by the "hot process" from the corresponding neutral oils and fats. Hence the process of manufacturing soap from soap stock fatty acids is very little employed in this country, in the United States, or in France. In other countries where the demands of the public as to colour and hardness of soaps are less rigorous, this process has gained some ground, especially in those small establishments where the recovery of glycerin from soap lyes (see below) is supposed to be too cumbersome. But even there it is not denied that soaps made from "deglycerinised" material cannot compare favourably in quality with those manufactured from natural oils and fats by the hot process, and the conviction is gaining ground that by adopting "deglycerinised" material, the soap is being made subsidiary to the recovery of glycerin, and is practically relegated to the position of a by-product.

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[1] French patent 333,974 (Gebrüder Haas).

[2] United States patent 424,991 (E. D. Mellen, 1890); German patent 158,929 (W. Heckhausen, 1904).

[3] French patent 348,708 (Ferrier).

With regard to the merits or demerits of the several soap stock fatty acids, it may be added that the autoclaved material has a paler colour than the material obtained by the *Twitchell* process, but is darker than that made by the ferment process. The loss of fatty material in the *Twitchell* process is practically *nil*, in the autoclave process it is very small, whilst in the case of the ferment process it is no longer negligible, a notable amount being lost in the middle layer. The soaps obtained from material prepared by the *Twitchell* process are the darkest. For this reason this process cannot be recommended for making "genuine" soaps; it is essentially a process that produces material for low-class soaps. (With regard to the suitability of the "deglycerinised" materials for the manufacture of soft soap, see below.) The most suitable material for preparing soap stock fatty acids by the autoclave process is that which is almost neutral, and which has not undergone a chemical bleaching process, whilst material high in free fatty acids or which has undergone a bleaching process is better adapted for being worked up by the *Twitchell* process. Material rich in free fatty acids, especially in volatile acids, is not suitable for the ferment process, which works best with good raw material (like the autoclave process). However, it must be pointed out that tallow and other high-melting fats are unsuitable for the ferment process, and if these materials are required, they must be "softened" by the admixture of low-melting fats, in order to become accessible to the action of the ferment.

None of these processes have been able to displace the boiling of neutral glycerides; nor are they likely to do so in the near future. Although one or the other or all of the three processes may be worked on a small scale, they are only employed for dealing with special material adapted to the making of special soaps, and those of inferior quality. Many installations erected for the production of soap stock fatty acids have been laid idle within the author's experience, after practical results had demonstrated that first-class soap could not be obtained from such material.

The manufacture of soap exclusively from rosin hardly falls within the operations of a soap-works, as rosin soap is of too soft a consistence to be used as a substitute for the ordinary household soaps and textile soaps. In soap-works rosin is therefore only used as an admixture to fatty raw material.

Soap made from rosin only is, however, largely used in paper mills, for sizing.[1] In these works rosin soap is frequently prepared with sodium carbonate alone, by boiling a dilute solution of sodium carbonate with rosin. No "fitting" is necessary, for the concentration of the rosin soap solution is regulated by the requirements of the works. Sodium carbonate not being capable of converting rosin completely into soap, these solutions represent an emulsion of true rosin soap and unsaponified anhydrides.[2] A discussion of the patents taken out for the preparation of rosin soap falls outside the scope of this work. The proposal to make a rosin soap by melting rosin and introducing dry soda into the melted mass [3] in the same manner as "fused" driers are prepared (see p. 147) cannot be recommended.

(C) SOAP-MAKING BY DOUBLE DECOMPOSITION OF SALTS OF FATTY ACIDS WITH SODIUM SALTS

(a) *Calcium Soaps with Sodium Carbonate.*

The old process for the manufacture of hard soaps by saponifying the oils and fats with causticised plant ashes and subsequently salting out the potash soap so obtained with common salt is, of course, a process of double decomposition. Cp. p. 315.

The process of saponifying oils and fats with lime (cp. Vol. I. Chap. II.), and subsequently converting the lime soaps, after removal of the glycerin, into soda soaps by double decomposition with sodium carbonate, was first proposed by *Tardani*.[4] This process has, however, never been adopted in practice. *Krebitz*,[5] evidently in ignorance of

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[1] German patent 203,713 (E. Fues); Mitscherlich, German patent 220,066.

[2] Von Possanner, *Papier-fabrikant*, 1910 (8), 221.

[3] Marcel Douxami, *Les Corps gras*, 1907, 242.

[4] English patent 1614, 1874. In place of lime, lead oxide is suggested; cp. also German patent 55,110.

[5] German patent 155,108; French patent 337,509; English patents 4092, 1905; 27,297, 1911.

Tardani's specification, brought this method into a workable form. He avoids the chief difficulty presented by the hardness of the lime soap, in that he conducts the saponification process at a carefully regulated temperature (from 98° C. to 100° C.), and does not protract the boiling with lime up to the point at which hard lime soap—" rock " —separates out, as is done when this process is applied to the production of candle-making material (see p. 220).

The saponification is effected by boiling oils and fats with 12 to 14 per cent of carefully selected lime of high purity (free from magnesia). The mass is stirred vigorously, and when a thorough emulsion has been produced, the vessel is covered to protect it from loss of heat. The product is allowed to stand for six to ten hours, when it presents the appearance of a solid, porous mass,[1] which is still sufficiently warm to permit its being dug out of the containing vessel. It is then thrown into a grinding machine, which disintegrates it to a powder. This powder is transferred to a cylindrical vessel, where it is repeatedly lixiviated with water, to wash out the glycerin contained in the mass, and is finally sucked dry by means of an air-pump.[2] The lime soap is transported to the soapery proper, and introduced in small quantities into a soap pan containing a boiling solution of sodium carbonate. When the decomposition of the lime soap is nearly complete, a small quantity of caustic soda solution is added. The soap-paste is next treated with salt, until the curd is thrown out. The contents of the soap pan are then allowed to rest, when calcium carbonate settles out at the bottom of the pan as a heavy sludge, whereas soap curd separates on the top ; a salt solution containing an excess of alkali forms an intermediate layer. The calcium carbonate sludge is drawn off, and, as it holds soap entangled (from 4 to 7 per cent), it must be washed, and finally lixiviated with water in a filter press, to recover the occluded soap. The soap left in the pan after drawing off the spent lye is reboiled, and finished in the manner described above under (*a*).

This process is an extremely cumbersome one. As pointed out already, the lime employed must be of great purity, and its amount must be greater than the theoretical quantity of 9·2 per cent (see Vol. I. Chap. II.). The manifold operations prior to the soap-making proper, and the repeated washings of the sludge necessary to recover the entangled soap, entail manipulations which compare very unfavourably with the simplicity of the " hot " process described under (*a*). If there be added to these drawbacks the difficulty of disposing of the lime sludge, it appears extremely unlikely that this troublesome process will meet with extended application. Moreover, it must not be overlooked that the finished soap contains some lime which greatly depreciates its quality, and that some soap is lost in the lime sludge.

Several years ago (when prices of glycerin were high) the process was adopted by some small soap-works, which had up till then run their spent lyes to waste. As the caustic lime exercises some purifying action in the case of low-class material (such as bone fat) containing albuminoids and gluey matter, this process may continue to be practised with low-class material under certain favourable commercial conditions. *G. A. Wrisley,*[1] however, states that the process has been worked with good results in Chicago.

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[1] It has been pointed out above (p. 220) that *Ferrier* claims the production of a similar lime soap, by saponifying with lime in a vacuum (French patent 366,460).

[2] Vogt, French patent 437,414.

A further patent by *Krebitz*[2] claims the manufacture of hard (or soft) soap from lime soap by double decomposition of the latter with ammonium carbonate in the presence of sodium chloride or sodium sulphate (or of potassium chloride or potassium sulphate), when the ammonium chloride or ammonium sulphate formed is said to be recovered completely. The patent specifications state that the operations are conducted in closed vessels. *Barbé, Garelli, and Paoli*[3] saponify the fats with aqueous ammonia under pressure, then convert the ammonia soap into soda soap by treatment with sodium chloride. For a description of the plant required, for which patent rights are claimed, the reader must be referred to the patent specifications.[4] It may be pointed out here that *Polony*[5] in 1887 had already patented the production of soda soaps by the interaction of the ammonia soaps with sodium chloride. In a later patent[6] only a small amount of ammonia—from 0·4 to 0·7 per cent—is added to the autoclave. This acts as a catalyst inducing hydrolysis, as does the small amount of lime used in the ordinary process.

Attempts have been made to bleach low-class "off-coloured" soaps by the same means that have been suggested for the bleaching of oils and fats (see Vol. II. Chap. XIII.). Thus, it has been proposed to add sodium persulphate to the mass in the soap kettle before it is completely saponified.[7] Sodium persulphate and hydrosulphite are also used for bleaching soap and are sold for this purpose under various fancy names. For the bleaching of the dark-coloured under layer ("nigre") 10 per cent of a 10 per cent solution of stannous chloride has been used. The remark made in Vol. II. Chap. XIII. with regard to oils and fats, viz. that the colour reverts after some little time, also holds good for soap treated with many bleaching agents, which latter are offered mostly under fancy names, since the problem of bleaching "off-coloured" soaps has been revived in consequence of the appearance in the market of soaps made from soap stock fatty acids.

The use of hardened (hydrogenated) fats now coming into vogue for the purposes of soap-making has been adversely commented upon by several observers,[8] particularly as regards fish and blubber oils, it being stated that soaps prepared from such hardened oils exhibit inferior lathering properties, and also that their colour and smell are inferior to soaps made from high-class materials. It is too early as yet to express a decided opinion on their merits, but it is difficult to see what valid objections can be raised against them provided they are prepared from good-class raw materials, *i.e.* materials which do not contain large amounts of unsaponifiable matter or oxidised acids.

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[1] *Journ. Ind. Eng. Chem.*, 1916, 8, 732.

[2] German patent 189,685; French patent 369,523; English patent 4092, 1905; United States patent 1,126,737, 1915.

[3] English patents 12,210, 1907; 9758, 1908; 24,836, 1908; 24,837, 1908; 24,838, 1908; German patent 209,537; Hungarian patent 40,217; French patents 372,341; 9255; Belgian patents 200,595; 207,823; Italian patents 182,832/201/229, 1906; 84,747/201/229, 1907.

[4] See also an article by F. Garelli, *Giorn. Chim. Ind. Appl.*, 1921, 3, 487.

[5] German patent 43,340.

[6] P. Barbé, G. de Paoli, F. Garelli, and Soc. Ammonia Italiana, French patents (A) 476,470, and (B) 476,471, 1914.

[7] Wiedermann and Vereinigte, Chem. Werke, United States patent 968,438.

[8] Hauser, *Seifensieder Zeit.*, 1913, 141. Cp. also Leimdörfer, *ibid.*, 1913, 1307.

Soaps made from greases, such as soap made from cotton seed stock (which has acquired a certain importance in commerce), will be incidentally referred to under Chapter XVI.

In the above-given description of the manufacture of genuine soaps, regard has only been had to the production of the best soaps that can be made by boiling in a soap pan, as these soaps are at present gradually ousting all inferior kinds of soap out of the market. Soap of this kind contains 63 to 64 per cent of fatty acid when freshly made (see p. 325), and approximately 30 per cent of water ; the amount of saline impurities such as salt, etc., being very small. Soaps made by this process are known as "*genuine*" soaps, and, with special reference to the process by which they are made, are termed in technical parlance "*settled*"[1] soaps (French—*Savon liquidé, Savons levés sur gras* ; German—*Geschliffene Seife, abgesetzte Seife, Seife auf Leimniederschlag*).

Next in purity to the genuine soap rank those soaps which are "boiled on a lye," and are termed "*curd*" soaps (French—*Savon levés sur lessive* ; German—*Seife auf Unterlauge*). They are "fitted" in such a manner that a somewhat open-grained soap—*curd*—rests on a lye, which, in the case of the best class of soaps, consists of a salt solution containing only small amounts of caustic soda or sodium carbonate. The water in these "finished" soaps contains larger quantities of salt than is the case with genuine soaps, and therefore the percentage of fatty acids barely reaches 63 per cent. If the fatty raw materials and the lyes are pure, a separation of dark soap (impurities) between lye and soap cannot take place ; but if the fatty materials, etc., are somewhat impure, a small layer of dark soap separates between the "curd" and the lye. This layer is left in the pan to be dealt with in a subsequent operation.

If the fatty material used in the making of curd soaps is of somewhat low quality (kitchen grease, bone fat, etc.), it is necessary to finish on lyes somewhat stronger in caustic alkali. The impurities, such as metallic soaps, etc., have not the same facility to settle out in the pan, as in the case of best soaps, in consequence of the curdy nature of the soap flakes. Hence the impurities segregate on cooling in the form of veins in the soap, and cause the solidified soap to exhibit a slight "marbling" or "mottling." These soaps are therefore known as "*genuine mottled*" soaps. Since this class of soap, as stated already, is mostly "finished" on strongly alkaline lyes, the "finished" soaps are much more strongly alkaline than those described above. The proportion of fatty acids in the soap is, therefore, liable to be still further reduced, viz. to about 61 per cent. As these soaps are too strongly alkaline for household use, they are chiefly employed for laundry and manufacturers' purposes.

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[1] The term "fitted" soap does not appear suitable, as lower kinds of soap, such as semi-boiled soap and blue mottled soap (*Eschweg soap, Savon de Nantes*) are also "fitted."

A lower quality still than "*genuine mottled*" soap is the type represented by the so-called *Marseilles soap*. This soap was originally made with lyes obtained from "barilla" and "kelp" soda, which contained a considerable amount of impurities, such as sodium carbonate, sulphates, sulphides, etc. The soap stock was previously an inferior kind of olive oil; now the lowest kind of olive oil and extracted sesamé oil are used. The amount of natural impurities from both fatty material and lyes (which latter were specially rich in sodium carbonate) retained by the water left in the "curd" was therefore much greater than in the case of the above-described soaps. These impurities segregated on cooling in the soap, just as is the case in the genuine mottled soap, but, being present in much greater quantity, they imparted to the finished soap a much more developed marbling. This marbling was made more prominent still by the addition of some iron sulphate ("copperas") or (and) English red. Thus "*savon bleu pâle*" and "*savon bleu vif*" respectively were obtained. It was well known that by adding more water to a soap of this kind the "marbling" would drop out (as in the case of "semi-boiled" soaps). Hence the "marble" was considered a sign of purity, and for many years the mottled appearance was looked upon by the public as a guarantee of good quality. The Marseilles soap contains, as a rule, not more than 60 per cent of fatty acid, but usually about 57 per cent, and in order to give it sufficient hardness for handling, it must be "pickled" in a brine solution. In the author's opinion a soap of this kind must be classed as a "filled" soap. The manufacture of this soap is practically confined to Marseilles; and even there the demand for it is greatly diminishing.

The repute which this soap enjoyed led to the production of another kind of mottled soap, with which the Marseilles soap must not be confounded, and which in the author's opinion must be looked upon as an "adulterated" soap. This imitation Marseilles soap, known as "*blue mottled*" soap ("*Eschweg soap*"; *savon marbré de Nantes*) ("*savon marbré nantais*"), is still a "fitted" soap, inasmuch as its proportion of fatty acids is a definite one, lying between 46 and 48 per cent, and cannot be varied at will (as is the case with the soaps to be described below). This soap is made by "filling" the genuine soap-paste with solutions of sodium carbonate, sodium silicate, and (or) salt, which vary both in strength and in their several proportions according to the nature and composition of the fatty raw material used. Mottled soaps are also made on the Continent by the cold process. They are stated to contain up to 20 per cent of the fat stock of tallow or bone fat.

Mottled soap made by the hot process represents at the boiling temperature a mixture of two soap solutions,[1] so carefully balanced[2] by the art of the soap-maker that they have approximately the same specific gravity at a temperature slightly below the temperature at which the soap has been finished. Hence, on solidification of the mass, no separation of the components into two distinct layers takes place. What separation does take place occurs so slowly that the solution which is richer in soap solidifies and imprisons the solution which is poor in soap, before the latter has had time to segregate in the form of a lower layer. Hence the desired " marble " in the soap is obtained.[1]

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[1] Cp. A. A. Shukoff, *Seifensieder Zeit.*, 1901, No. 22; Leimdörfer, *ibid.*, 1906, Nos. 24 to 29; Merklen, *Études sur la constitution*, etc.

[2] If the "balancing" is not done correctly the mottle does not "strike," and the finished

The marbling is made more pronounced by the addition of ultramarine or " copperas " for blue mottled soap; by using other pigments (lamp black and English red respectively) grey mottled and red mottled soaps are produced.

Such soap also requires " pickling " before it is put on the market.

This soap can be boiled direct from neutral fats in one operation, when, of course, the glycerin remains in the soap. But it is more profitable to the soap-maker to remove the bulk of the glycerin by saponifying the whole or part of the fatty material in a separate pan, thus obtaining a " glycerin lye " and curd soap, which is then converted into mottled soap. The colour of the finished soap does not suffer thereby, whereas soap made from " soap stock fatty acids " frequently becomes so seriously discoloured that it is practically unsaleable.

The lowest kind of " fitted " soaps are those which are termed " semi-boiled " soaps (French—*Savon mi-cuit*; German—*Leimseifen, Seifen auf halbwarmen Wege*). These soaps are nothing but more or less concentrated saline solutions of soap, and can be made to contain any desired proportion of water. Some kind of purification is effected by allowing these soaps to drop a certain amount of " nigre," containing a good deal of the impurities in the raw material; but, as a rule, these soaps are mostly filled into frames immediately after being made. The manufacture of these soaps may be considered as entirely obsolete, all the more so as the glycerin contained in the fatty raw material is lost, much as in the making of soft soap from glycerides; indeed, these soaps may be likened to best soft soaps. At present small quantities of this class of soap are still made in the south of Europe from low-class fatty material, rich in free fatty acids. This kind of soap must, of course, be considered as " adulterated " soap.

In this country " adulterated " soaps are mostly prepared by the aid of the mixing (crutching) machines into which " neat " soap settled on a nigre is run, and is there incorporated with solutions of salt, sodium carbonate, and (or) sodium silicate to any desired extent, so that all grades of soap ranging from 60 per cent of fatty acids downwards to even 10 per cent can be, and are, made. In order to give these soaps sufficient firmness for handling they are either " stoved " or " pickled," as the case may be.

In mitigation of the practice of " filling " soaps with solutions of

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soap represents either two layers or a uniformly " mottled " mass without any sign of " marbled veins."

[1] Lewkowitsch, " Modern Views on the Constitution of Soap," *Journ. Soc. Chem. Ind.*, 1907, 590.

sodium borate, or of sodium carbonate, or (and) silicate is adduced the apologetic explanation that, besides hardening the soap, the added solutions possess detergent properties. The best that can be said for soaps of this class, which range in their proportion of fatty acids between 52 and 60 per cent, is that they might be considered as standing on the borderland between genuine soaps and "adulterated" soaps. They should be openly described as "filled" soaps.

Silica is deposited in the fibres during washing, and damages the washed goods by its mechanical grinding action, hence it should not be contained in textile soaps.

There can, however, be no doubt that adulteration has taken place in the case of those "filled" soaps which have been "loaded" with weighting substances, such as clay, talcum (sometimes sold under the name of "fillers"), chalk, barytes, asbestos, seed husks, etc., or with solutions of magnesium salts, etc. In the same category fall soaps filled with starch. In the opinion of the author soaps containing less than 50 per cent of fatty acids should be looked upon as "adulterated," whether the "fillings" have detergent properties or not, unless the admixture be declared openly (see below "Sand Soaps"). Detergent compositions formed by the union of silica and alumina with soda have been patented.[1] The patentee claims that these compounds, one of which is stated to have the formula $Al_2Si_3Na_8O_{13}$, may be used either alone or in combination with soap.

Before the manufacture of genuine soaps had reached the high state of perfection to which it has attained at present, the not inconsiderable amount of free caustic soda present in the ordinary household soaps forbade their use for toilet purposes. Hence for the production of toilet soaps, curd soap made from carefully selected material was subjected to refining processes of which the simplest was that which produced "remelted soaps." More complicated are the methods for making milled soaps and transparent soaps. These three processes are still in vogue at present.

Remelted Soaps ("*Savons par refonte*").—The process consists in bringing curd soaps back into the liquid state by "remelting" in steam jacketed vessels; by reworking the soap, free caustic soda is converted into carbonate, and thus rendered less harmful to the skin.[2] (This process of "remelting" is, in some cases, repeated several times. At the same time colouring matters, ethereal oils (perfume), and medicaments (in the case of medicated soap) are incorporated with the liquid mass in the last stages of the process, and the soap is then run into shallow trays or moulds, to be stamped after solidification. The remelting used to be done in this country in separate establishments (the existence of which was due to the revenue tax on soap) by special manufacturers who were known as "soap remelters," in contradistinction to the "soap-makers," who supplied the curd soap. At present the "remelted" soaps are chiefly made by the soap-makers themselves, who take the finished soap, whilst still hot, from the soap pan, and colour and perfume it. The soap is then allowed to cool in small frames, much in the same manner as the household soaps are cooled. Remelted soaps contain approximately the same amount of water as household soaps do.

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[1] Kayser, English patent 6934, 1909.

[2] Other patented methods of neutralising free caustic soda are: addition of ammonium salts (C. A. Wright, English patent 14,681, 1885), of egg albumen (German patents 112,456, 122,354, 134,933), wheat-gluten (Klopfer, English patent 10,350, 1904), casein (Horn, German patent 193,562); Runge, English patent 22,441, 1908; German patent 221,623; but it may be added that they are superfluous if due care be observed in the manufacturing process.

Milled Soaps ("*Savons broyés*").—The name is derived from the milling processes through which these soaps are passed. The "basis" for these soaps is a carefully made "*curd*" prepared from best materials and "finished" so carefully that the amount of free caustic soda is extremely small. In order to render the raw material suitable for milling, the bulk of the water must be removed. This is done by cutting the soap bars into fine shavings by means of a rotary cutting machine, and spreading the shavings in thin layers on trays in a steam-heated drying chamber. In large establishments the shavings are carried on an endless band through a drying apparatus. The soap shavings thereby lose about 20 per cent of water, and are then ready to be worked into fine shreds between granite rollers in a milling machine (or crushing machine). At this stage of the operations colouring matters, glycerin, and perfumes are introduced. As the operations take place in the cold, and the soap is only slightly warmed, much more delicate perfumes can be used than in the "remelting" process. Medicaments (for "medicated" soaps) are also incorporated at this stage.[1] The mass is repeatedly passed between the rollers until a complete intermixture is obtained.[2] Continental toilet soaps are frequently "filled" with vegetable products like tapioca meal. Casein [3] is also used as a filling agent. The shredded soap is then transferred to a "plodding" machine ("*peloteuse*"), in which the shreds are compressed by means of a helical screw and driven against a plate perforated with a number of small holes, so that the soap passes this part of the machine in the form of single thick threads. Beyond this plate the threads, still under pressure, traverse a jacketed chamber, heated by hot water, and are thus pressed together at a somewhat elevated temperature, so that the threads coalesce and leave the machine in the shape of a continuous bar of soap, which is cut into cakes of suitable size for the stamping machine. A special kind of milled soap is "*shaving soap*"; the "basis" for these soaps is mostly made with both caustic soda and caustic potash, in order to produce a finer texture and better lathering properties.

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[1] In order to guard against the presence of free caustic soda in the finished soap, some makers add olive oil or (and) wool-wax, on the assumption that the caustic soda will combine with them to form neutral soap. These soaps are known as "super-fatted" soaps (cp. also p. 364).

[2] The machinery for this purpose was first exhibited in 1855 by Lesage, founder of the firm Beyer Frères, who operated, however, on soft soap paste. An improved machine was shown in 1867.

[3] E. F. Rosseau, French patent 472,587, 1913. Cp. also *Journ. Soc. Chem. Ind.*, 1919, 29 R.

Transparent Soaps.—Genuine transparent soaps are prepared by shredding and drying the soap " basis," as described under " milled soaps," and then dissolving the dry shreds in alcohol. They may also be prepared by saponifying the oils and fats with alcoholic soda. Any impurities in the soap (*e.g.* sodium carbonate) settle out and can be withdrawn, or the alcoholic solution is decanted. The bulk of the alcohol is then distilled off, and the gelatinous residue is run into moulds, wherein the soap solidifies to a cake which still retains some alcohol and has a dull or only translucent appearance. On storing the cakes for some months, they lose most of the retained alcohol and become transparent, especially if kept at a temperature of 35° C. The " basis " of these soaps is made from tallow, coconut oil, and castor oil. Other kinds are made from tallow-rosin soaps, which may still be regarded as genuine soaps though they undoubtedly represent lower qualities. If the latter soaps are " filled " with sugar solution, they must be regarded as adulterated soaps approaching in quality the cheap transparent soaps made by the " cold " process, although they are, as a rule, freer from uncombined caustic alkali.

A special kind of transparent soap is made from stock containing very high proportions of rosin ; some qualities contain even free rosin acids. When such soaps are allowed to cool in a shallow layer they acquire transparency.

2. SOFT SOAPS—POTASH SOAPS

In the manufacture of soft soap the base used preponderantly is potassium hydrate, small quantities only, if any, of caustic soda being employed under certain conditions. Thus in summer it is the custom to saponify with a mixture of caustic potash and caustic soda, according to the desired consistence of the finished product. By using a fatty material of high melting point it is possible to prepare a solid potash soap. Thus *Worms* [1] uses as raw material a mixture of tallow and coconut fatty acids with the addition of Japan wax, Chinese wax, beeswax, spermaceti, or carnaüba wax.[2] It is claimed for these soaps that they give a strong and persistent lather. A solid potash soap containing 65-72 per cent of fatty acids is being sold in Germany.[3] The manufacture of potash soap is much simpler than that of hard soaps, as it involves practically only one operation, viz. " boiling " the glycerides with caustic alkali solutions in a pan, no salting out being required. Hence the resulting product, after being properly " fitted," can be run straightway from the boiling-pan into the vessels in which the soap is sold.

The method of manufacturing " genuine " commercial soft soap for household purposes differs, however, essentially from that employed in the manufacture of hard soap in that the presence of potassium carbonate is required so as to produce a soap of clear translucent appearance which possesses the desired consistence for handling.

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[1] German patents 248,657 ; 262,591.

[2] Müller, Austrian patent application, ausgel, 15, iv. 1910.

[3] *Seifensieder Zeit.*, 1911, 1389.

Before the production of caustic potash had reached its present state of perfection, in other words, before it was possible to obtain a pure caustic potash, the soap-maker prepared his potash lyes by treating wood ashes (or later on pearl-ash) with lime, leaving so much of the potassium carbonate undecomposed as prolonged experience had shown him to be required, and to be most suitable, for the obtainment of a properly fitted potash soap. As potassium carbonate is only required for the "fitting" operation, the best practice is to carry out the saponification of the glycerides by means of caustic potash of known strength and to add the potassium carbonate required in the course of saponification or at the finishing operation.

The following two tables, giving the amounts required theoretically for the saponification of glycerides, have been calculated by the author for use in practice (cp. p. 320):—

Caustic Soda Solutions required to saponify Fats of Mean Molecular Weight 670 (*Coconut Oil, Palm Kernel Oil*) [*Lewkowitsch*]

Weight of Fat in Tons.	Gallons of Solution of Caustic Potash.			
	20° Twaddell = S. G. 1·1.	40° Twaddell = S. G. 1·2.	60° Twaddell = S. G. 1·3.	71° Twaddell = S. G. 1·355.
·05	21·31	10·42	6·97	5·80
·1	42·63	20·84	13·95	11·60
·15	63·94	31·26	20·92	17·40
·2	85·25	41·68	27·90	23·21
·25	106·57	52·10	34·87	29·01
·3	127·88	62·52	41·85	34·81
·35	149·19	72·94	48·82	40·61
·4	170·51	83·36	55·79	46·41
·45	191·82	93·78	62·77	52·21
·5	213·13	104·20	69·74	58·01
·55	234·45	114·62	76·72	63·81
·6	255·76	125·04	83·69	69·62
·65	277·07	135·46	90·67	75·42
·7	298·39	145·88	97·64	81·22
·75	319·70	156·30	104·61	87·02
·8	341·01	166·72	111·59	92·82
·85	362·33	177·14	118·56	98·62
·9	383·64	187·56	125·54	104·42
·95	404·95	197·98	132·51	110·22
1·0	426·27	208·40	139·49	116·03
2·0	852·54	416·80	278·97	232·05
3·0	1278·80	625·19	418·46	348·08
4·0	1705·07	833·59	557·94	464·10
5·0	2131·34	1041·99	697·43	580·13
6·0	2557·61	1250·39	836·92	696·16
7·0	2983·88	1458·79	976·40	812·18
8·0	3410·14	1667·18	1115·89	928·21
9·0	3836·41	1875·58	1255·37	1044·23
10·0	4262·68	2083·98	1394·86	1160·26

Caustic Potash Solutions required to saponify Fats of Mean Molecular Weight 860 (*Tallow, Cotton Seed Oil, Olive Oil, etc.*) [*Lewkowitsch*]

Weight of Fat in Tons.	Gallons of Solution.			
	20° Twaddell = S. G. 1·1.	40° Twaddell = S. G. 1·2.	60° Twaddell = S. G. 1·3.	71° Twaddell = S. G. 1·355.
·05	16·60	8·12	5·43	4·52
·1	33·21	16·24	10·87	9·04
·15	49·81	24·35	16·30	13·56
·2	66·42	32·47	21·73	18·08
·25	83·02	40·59	27·17	22·60
·3	99·63	48·71	32·60	27·12
·35	116·23	56·82	38·03	31·64
·4	132·84	64·94	43·47	36·16
·45	149·44	73·06	48·90	40·68
·5	166·05	81·18	54·33	45·20
·55	182·65	89·30	59·77	49·72
·6	199·26	97·41	65·20	54·24
·65	215·86	105·53	70·63	58·75
·7	232·47	113·65	76·07	63·27
·75	249·07	121·77	81·50	67·79
·8	265·67	129·88	86·94	72·31
·85	282·28	138·00	92·37	76·83
·9	298·88	146·12	97·80	81·35
·95	315·49	154·24	103·24	85·87
1·0	332·09	162·36	108·67	90·39
2·0	664·19	324·71	217·34	180·78
3·0	996·28	487·07	326·01	271·18
4·0	1328·37	649·42	434·68	361·57
5·0	1660·47	811·78	543·35	451·96
6·0	1992·56	974·14	652·01	542·35
7·0	2324·65	1136·49	760·68	632·74
8·0	2656·74	1298·85	869·35	732·14
9·0	2988·84	1461·20	987·02	813·53
10·0	3320·93	1623·56	1086·69	903·92

Soft soap used to be made in fire-heated pans; but during the last two decades these have been replaced in modern works by pans similar to those used in the manufacture of hard soap, but fitted with a "close" steam coil in addition to an open steam coil or coils.[1]

The fatty raw material (see p. 314), which for the best soap consists chiefly or preponderantly of linseed oil, is introduced into the soap pan and churned up with steam, when a caustic potash solution of about 20° Twaddell is run in. Whilst the saponification proceeds, lyes of higher strength can be used. When all the glycerides have been converted into soap, and the latter is just slightly alkaline, potassium carbonate solution is introduced. The soap will then contain an excess of water; this is removed by turning off the open steam and heating the mass with the aid of the dry steam coil. At the same time the mass is agitated by a suitable mechanical arrangement so as to promote the rapid evaporation of excess of water. By taking samples and examining their appearance and consistence on a glass plate, the operator is able to judge exactly the point at which the soap is "finished." The mass then represents practically a mixture of potassium salts of fatty acids with a solution containing all the glycerin from the fats, a slight excess of caustic potash, and a certain amount of potassium carbonate. The two component parts of this mixture are so carefully balanced that on cooling a homogeneous mass is obtained which retains its transparency. If the soap is made from linseed oil only, the transparency will be retained even in winter, and the soap will not "congeal"; but if the soap stock contains notable amounts of cotton seed oil or even maize oil, and frost sets in, then the soap is liable to become dull ("blind"). Hence the choice of raw material is conditioned by the seasons. If some tallow is used in the stock, the harder potassium stearate or palmitate, or a mixture of both, crystallises out in starlike clusters, producing what is known in commerce as "figging" (cp. above, p. 331). The same effect can also be produced by replacing a portion of the caustic potash by its equivalent of caustic soda. It should be noted that as soda soaps are unable to retain as much water as do potash soaps, substitution of caustic soda for caustic potash somewhat reduces the yield of 240 parts of soft soap from 100 parts of glycerides. By collating the tables given on pp. 320 and 321 with those given on pp. 347 and 348, the equivalent amounts can be easily found. The more soda used, the more is the soft soap apt to lose its transparency. This holds especially good of that white soft soap, known in Germany as "silver soap," which is chiefly made from cotton seed oil.

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[1] Cp. Bauer, English patent 21,457, 1909.

In the soft soaps prepared in the manner described above all the glycerin is retained, and, as has been pointed out already, a certain excess of caustic potash and notably of potassium carbonate is necessary in order to give the soap the inviting appearance which the public demands.

By operating carefully, potash soaps can be made which are devoid of free alkali and potassium carbonate. Such soaps are, however, only manufactured for the purposes of the textile industry (see below), when absence of free alkali or of carbonate is essential, and the appearance of the soap is of no importance. In this case it is indispensable to work with pure caustic potash, as all impurities, such as sulphates, chlorides, and carbonates, pass into the finished soap.

Solutions, or frequently only emulsions, of soft soap are known in commerce under the name *liquid soaps*. Those used in surgical and in pharmaceutical practice,[1] as also those intended for cosmetic (toilet) purposes, are mainly alcoholic solutions containing certain proportions of glycerin and are clear solutions. The first-mentioned soaps may contain medicaments and antiseptic substances.[2] In most of these liquid soaps neutrality would appear a *desideratum*. This can be easily fulfilled by careful working, and it would appear unnecessary to prepare these soaps from fatty acids or rosin acids. For disinfecting purposes, aqueous solutions or emulsions of soft soap are sold under a large variety of fancy names. They contain tar oils (benzene, toluene) in such proportions that the solutions can be diluted with a certain amount of water without becoming turbid through the separation of the neutral tar oils (cp. also " Emulsified Oils "). Thus, the author has found in an aqueous solution of soft soap 55 per cent of crude tar acids. Solutions of soft soap containing terpineol are protected by *Fritzsche*.[1]

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[1] A. Holub, *Seifensieder Zeit.*, 1908, 1480; *Chem. Zentralbl.*, 1909 (1), 698.

[2] Thus liquid "sulphur" soap is made by passing a current of sulphuretted hydrogen into an alcoholic solution of soft soap (Sarason, German patent 191,900). Cp. Schmatolla, German patent 197,226; K. Lendrich, United States patent 895,477; S. Knopf, German patent 255,157; Fendler and Frank, French patent 419,235; English patent 17,100, 1910; Schmitz, French patent 419,649.

Potash soaps contain much larger quantities of water than do hard soaps. Genuine soft soaps made in the pan retain so much water that 100 parts of neutral glycerides yield 240 parts of commercial potash soap.

From these data the theoretical composition of a genuine soft soap can be calculated.

Suppose a fat of the mean molecular weight 860 has been saponified. Its saponification value is approximately 195, or, in other words, it requires 19·5 per cent of KOH (=16·42 per cent of K_2O) for saponification.

The 240 parts of potash soap obtained from 100 parts of such fat contain, of course, 16·42 parts of K_2O; therefore we have in the soap 6·843 per cent of K_2O [240 : 16·42 : : 100 : x].

As the mean molecular weight of the fatty acids is approximately 275, the corresponding figure for the fatty anhydrides is $275 - 9 = 266$. Since 47·1 parts of potassium oxide combine with 266 parts of fatty anhydrides, we have in the soap 38·7 per cent of fatty anhydrides [47·1 : 266 : : 6·843 : x]. The remainder consists of glycerol and water, potassium carbonate, and excess of caustic alkali, if any.

The composition of a genuine potash soap should, therefore, theoretically, be—

	Per cent.
Fatty anhydrides	38·700
Combined potassium oxide, K_2O	6·843
Glycerol, water, and potassium carbonate (by difference) .	54·457
	100·000

During the recent shortage of potash the genuine soft soap was replaced by a soap jelly made with soda and containing 10 per cent or even less of fatty acids.

Rosin is used for cheaper kinds of soft soap, just as in the case of hard soaps. For the reasons stated above (p. 314), soft soaps made with rosin as part of the stock, and intended for household purposes, are still looked upon as genuine.

In the manufacture of soft soaps for textile purposes rosin must be avoided; and the presence of rosin in such a soft soap must be considered as distinctly lowering its value, or even as constituting adulteration.

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[1] German patent 207,576.

Soft soaps, like hard soaps, are also "filled" ("thinned out") with solutions of potassium silicate, potassium carbonate, potassium chloride, carragheen moss decoctions, starch, and potato flour. The last two substances are largely used for the adulteration of opaque (white) soft soaps made on the Continent, especially the German "silver soap," in order to "increase the yield." The soap used by silversmiths is heavily filled, sometimes up to 60 per cent, with chalk. Talcum is unsuitable for this purpose.

In the best soft soaps all the glycerin is retained, and its presence helps to impart to the soap the desired transparency. The endeavour to recover this glycerin has led to the production of soft soap from fatty acids (oleic acid) and from "soap stock fatty acids."

Oleic acid lends itself best for the making of neutral soaps for manufacturers' purposes, as it is easy to prepare a completely neutral soap by bringing together a known quantity of oleic acid with the exactly required quantity of a solution of pure caustic potash. It has, however, been found by experience that these soaps do not impart to the woollen fibre the same lustre and "feel" which a soft soap containing all the glycerin from the neutral fats is able to give.

With the introduction of the "soap stock fatty acids" the production of soft soaps from these materials has gained ground, notably on the Continent. But the same strictures which have been made above with regard to hard soap made from such material may be repeated also in this case. High-class soft soaps such as are in demand in this country cannot be obtained with soap stock fatty acids. It need therefore only be pointed out briefly that, whereas the fatty acids obtained by the *Twitchell* process are entirely unsuitable for soft soap, those made by the autoclave process can only be used for the inferior qualities. Slightly better than the soap stock fatty acids prepared by the autoclave process is the soap stock material obtained by the ferment process. It should, however, be emphasised that such soaps are inferior to those made from glycerides. As the price of potassium carbonate is almost the same as that of caustic potash, or slightly higher, it would be unremunerative to neutralise the free fatty acids in the soap stock fatty acids with carbonate, as is done in the case of hard soaps made from this material (see above, p. 333). There is, therefore, no inducement to use potassium carbonate in place of caustic potash.

The process of making soft soap by double decomposition has been patented (see above, p. 338), but it is very unlikely that the manufacture of soft soaps by this process will ever be attempted.

Commercial Varieties of Soap

In order to suit various purposes, the variety of soaps that are being made is exceedingly great.

By far the largest quantities of hard soap are used for laundry, toilet, and other household purposes.

The most suitable soaps for laundries are either **genuine mottled** or "settled" tallow-rosin soaps. The best class of toilet soaps contain, as a rule, 80 per cent of fatty acids; but it must be understood that there are all varieties in commerce, down to the cheap transparent toilet soaps, which contain even less than 40 per cent of fatty acids. As pointed out already, medicaments, etc., are frequently incorporated with soap in the milling machine, and thus an enormous variety of **medicated soaps,** or soaps containing plant extracts, disinfectants, with or without chlorinated hydrocarbons, carbolic soap, etc., are made.

For household purposes all qualities are made, from genuine soap containing 63 per cent of fatty acids down through all gradations of **carbonated, silicated, "filled," "run"** soaps to **"scouring"** soaps which may contain only 10 per cent of fatty acids.

Soaps made from coconut or palm kernel oils have the property of lathering in water containing salts ("marine soaps"). *Buchanan*[1] prepares a marine soap by incorporating soda soap with a proportion of potash rosin soap. *Soulier and Reisdorff*[2] patent a detergent composition for use with sea water prepared from purely inorganic materials (silica, alumina, and soda).

Special objects are served by **floating soaps,** made by incorporating air with soaps whilst still in the pasty state or by mixing oxygen-yielding bodies, like hydrogen peroxide, with the molten soap;[3] **disinfecting soaps,** containing carbolic acid, "anthrasol" formaldehyde, terpineol, etc.; soaps containing aromatic derivatives of mercury have been patented by *Farbenfabrik, vorm.: F. Bayer and Co.*[4] **Sand soaps** are made chiefly from finely ground silica or infusorial earth, by mixing it with hard soap (and sometimes with soda), so as to allow the mass to be shaped and handled like a soap cake. Admixture with sawdust has also been proposed for the same purpose.

During the last decade *shredded soaps*, made from genuine soap, and *ground soap*, also made from genuine soap, have come into vogue. These soaps may be considered as representing the best class of **dry** soaps;[5] they contain more than 64 per cent of fatty acids and may reach as high a content as 80 per cent. Usually, however, under the name of **dry soaps** are understood those **washing powders** and **soap powders** which are prepared by grinding together hard soaps with sodium carbonate.

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[1] English patent 27,083, 1908; cp. also Lever Brothers, Ltd., French patent 405,943.

[2] French patent 413,964.

[3] Föll, Austrian patent application 2773-06.

[4] German patents 233,437, 246,880; English patents 10,075, 1909; 24,981, 1910; French patent 402,740, and additions 13,062, 13,682; cp. also Meister, Lucius, and Brüning, German patent 271,820; Schrauth and Schoeller, German patent 216,828.

[5] For the manufacture of a dry soap, in form of powder, by blowing hot soap under pressure into a chamber, wherein it settles out as a fine powder, cp. O. Lindemann, English patents 25,276, 1907, 26,133, 1908, and Gebr. Körting, German patents 203,193, 232,698. The preparation of finely divided soap by pouring soap in a liquid condition into brine is claimed by A. H. Finlay (English patent 12,849, 1907). With regard to a machine for the mechanical preparation of finely divided soap, cp. German patent 200,264 (Wecker and Buhler); United States patent 900,967 (W. Tillson); Riggs, English patent 20,952, 1910; Schwartz and Ayres, United States patent 1,033,737. "Flake" soap is also produced by cooling hydrous soap between rotating, strongly cooled cylinders to a band which is cut up into shreds and flakes by mechanical means (German patent 223,659, Flakes, Limited).

On account of their handiness, and even economy, these soaps have come into extensive use, and are therefore manufactured in increasing quantities. They are made by preparing a genuine or other soap stock, and grinding this under edge-runners together with soda crystals or soda ash and a suitable proportion of water or soap solutions, made by boiling "oleine" with caustic soda solution. The ground mass is then reduced to powder in a disintegrator. Other methods are also in vogue. A machine for performing the saponification of oils and fats, subsequently drying them, and reducing the soap to powder, has been patented by *C. Ellis*.[1] The amount of real soap varies considerably. In the United States cotton seed soap stock is largely used for making such washing powders (cp. Chap. XVI. p. 418), but these are much inferior in quality to soaps made from better material, such as palm oil. (It should be pointed out that dry soap dust is liable to cause explosions.[2]) Vegetable saponins are sometimes incorporated with dry soaps in order to increase the lathering properties, as also are the protein-containing germs of various cereals,[3] and brewery yeast.[4] The addition of borate of ammonia has been patented.[5] Frequently inert matter such as sodium sulphate, kieselguhr, magnesium carbonate,[6] etc., is incorporated with the soap powder. Sodium silicate is also added to some varieties of soap powders.

Mixtures containing *no* soap (*i.e.* a mixture of sodium perborate, soda, and borax) fall outside the scope of this work. In order to make soap cakes which will dissolve easily in water it has been proposed to press the powdered soap into cakes after the addition of a suitable agglutinant such as dextrine.[7] The manufacture of soap containing glyceryl borate has been patented by *Grant*.[8]

Very considerable quantities of soap are used in the textile industries, notably in the silk, woollen, and cotton industries. These soaps, known as **textile** soaps, form, as it were, a special group, and require therefore brief consideration.

In the *silk industry* the soap used for degumming the raw silk fibre is mostly made from olive oil or (chiefly in America) from lard oil. The soaps intended for this industry are required to be as free from uncombined alkali as possible, as it is said that even the smallest amount is apt to damage the "feel" and lustre of the silk. Nevertheless, silk manufacturers add a small amount of potassium carbonate to the soap bath. For washing finished silk goods it is advantageous to have an easily soluble soap. Olive oil soda soap, and especially oleic acid soda soap, are in vogue for this purpose. Addition of borax to such soaps is sometimes desired by the silk manufacturers.

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[1] United States patents 904,520; 1,007,680.

[2] Cp. S. F. Peckham, *Journ. Soc. Chem. Ind.*, 1907, 244.

[3] Macpherson and Heys, English patents 5620, 1909; 20,089, 1909; French patent 415,974; Murray, French patent 440,978; Klopfer, English patent 2191, 1912; Lothammer, French patent 432,025; Macpherson, Brondesbury and W. E. Heys, English patent 8478, 1915. Cp. also M. Aisen, United States patent (A) 1,360,252, (B) 1,360,253, (C) 1,360,254.

[4] Anyon, United States patent 1,064,591.

[5] Armstrong, English patent 17,218, 1904.

[6] Walker and Freestone, English patent 17,228, 1909.

[7] Saponia-Werke, F. Boehm, French patent 417,139; Patent Borax Co., English patent 13,008, 1910.

[8] French patent 417,547.

In the *woollen industries* [1] soap is used (*a*) for scouring raw wool, (*b*) for scouring spun yarn, and (*c*) for scouring the woven woollen fabric.

(*a*) Soap intended for *scouring raw wool* should not contain free caustic alkali, as free alkali acts injuriously on the wool, destroying its surface by pitting the scales and taking away its lustre. Some wool-washing establishments wash therefore with dilute ammonia solutions or with ammonia soaps. If the raw wool is of inferior quality, no objection is taken to a small amount of alkaline carbonate.

Soft potash soap is preferable to soda soap, *cæteris paribus*. Unsaponified fat, unsaponifiable matter, rosin, silicate, and "fillers" should be absent. "Secret powders" consist largely of sodium carbonate and inert substances with a minimum of palm oil soap or even cotton seed oil soap.[2]

(*b*) Soaps for *scouring spun yarn* should also be neutral. For the best class of goods the soap is made from sulphur olive oil (see Vol. II.), but genuine mottled soaps (see above) are very largely employed, as they can be made to contain but a small quantity of free caustic soda. Rosin and (or) cotton seed oil (or coconut oil) should not be used for these soaps, nor should silicate, etc., be employed.

(*c*) Soaps for *scouring*, "fulling," "milling" *the woven woollen fabric* for best-class goods should be devoid of free alkali. For the first two purposes, *cæteris paribus*, potash soap is preferable to soda soap. This should be made from pure olive oil or tallow. To the latter some coconut oil is usually admixed.

For the scouring of low-class goods, such as union goods for which mungo and shoddy are used, strongly alkaline soaps are demanded by manufacturers, and a certain amount of free caustic alkali and alkaline carbonates is allowed. Silicate and rosin should, however, be absent; neither should the soap contain unsaponified fat nor unsaponifiable substances.

In the *cotton industry* soap serves to remove "stiffening," and is used for washing the dyed or printed fabric. Soaps for the use of *calico printers* are mostly made from olive oil or palm oil. Small quantities of coconut oil are also used. They should not contain maize oil, cotton seed oil, or rosin; neither should they contain free alkali, as this acts injuriously on the colour of the printed calico.

The textile soaps described above are (or should be) genuine soaps, unless filling with sodium carbonate and silicate is allowed. As special textile soaps may be mentioned :—

Softening, "Cotton Softener."—These soaps are used in the cotton industry, and consist of a salve-like emulsion made by incorporating large quantities of water with genuine soap. "Softening" is, as a rule, made from coconut oil or from tallow, and "run down" with water to contain even as little as 20 per cent of fatty acids. This soap is frequently "filled" with starch or potato meal. In some "softenings" potash soap is substituted for soda soap.[1] In the United States "softening" is frequently made from maize oil and cotton seed oil. Another type of "softening" is an emulsion consisting of carragheen moss and coconut oil (or palm kernel) soap, to which sometimes glycerin is added.

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[1] Cp. Lewkowitsch, *Journ. Soc. Dyers and Colourists*, 1894, 42; *Journ. Soc. Chem. Ind.*, 1894, 258. Cp. also Massot, *Zeits. f. angew. Chem.*, 1906, 233.

[2] Cotton seed oil should be avoided in the making of textile soaps. Nevertheless, large quantities of cotton seed soap stock are shipped from the United States to this country and are used for scouring inferior goods (see Chap. XVI.).

Liquid Soaps

Soap Emulsions.—These are prepared by partially or completely neutralising Turkey-red oil with caustic alkali.[2] A solution of soap in carbon tetrachloride[3] or chloro-ethylenes[4] belongs to this group. Cleaning emulsions containing no soap in which the carbon tetrachloride and water are emulsified by means of a small amount of saponin, have been patented by *Wackenreuter.*[5]

Dry Cleaning Soaps—Benzin Soaps.—These soaps are made from potash soaps, containing only small quantities of soda soap, or from oleic acid and ammonia and petroleum naphtha (or even burning oil which is, however, difficult to remove), or ethyl acetate.[6] Commercial specimens of such soaps examined in the author's laboratory contained approximately 30 per cent of hydrocarbons. These soaps form a gelatinous mass, and are specially used in the "dry cleaning" trade.[7] The best soaps of this class contain free unsaponified fat so as to ensure absence of free alkali.

The facility with which foreign substances can be incorporated with, and are retained by, solidified, jellified, or **liquid soap** has led to the production of an enormous amount of all kinds of "special" soaps for each of which some valuable property (real or supposed) is claimed. It is quite impossible to give a classification of these, and it must, therefore, be left to the analyst to decide, in each individual case, whether a soap containing foreign substances must be considered to be an adulterated soap or not. Thus a soap sold as a *sand soap* or *pumice soap*[8] is not adulterated soap. Nor would a soap containing naphtha, or petroleum, or tar oils, or sulphur, or peroxides,[1] or perborates,[2] or sodium tungstate,[3] or lithium salts,[4] fall under this head, if sold as *naphtha soap, petroleum soap, tar soap, or sulphur*, etc., *soaps*.[5] It should, however, be pointed out that, as a rule, these substances are very frequently accompanied by loading materials (especially sodium silicate solutions). In this connection it may be mentioned that under the name of "American soap stock" there is sold a heavy mineral oil, mixed with soap and in some cases even with "oleine."

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[1] Cp. F. C. Burnham, *Journ. Soc. Chem. Ind.*, 1906.

[2] Cp. L. E. Common and Hull Oil Manufacturing Company, English patents 23,768, 1906; 16,969, 1907; cp. also C. H. Meyer, German patent 197,400 (cp. p. 215); Soc. Nauton Frères et de Marsac and T. F. Tesse, English patent 9441, 1909; German patent 236,295.

[3] Stockhausen, German patent 169,930; cp. *Chem. Zeit.*, 1908, 935; Armstrong, English patents 16,406, 1905; 21,280, 1908; Drayer, United States patent 1,049,495; Schmitz, German patent 255,901; Welter, French patent 402,175; English patent 8982, 1909.

[4] French patent 396,493 (Stockhausen and Traiser); Koller, English patent 15,288, 1910; United States patent 1,038,900; Soc. Nauton Frères et de Marsac and Tesse, English patent 14,725, 1909; Fendler and Frank, English patent 17,100, 1910.

[5] United States patent 1,038,783.

[6] Stockhausen and Traiser, German patent 246,606.

[7] Cp. German patent 92,017. Gartenmeister, Simon, and Dürkheim, German patent 267,439; de Sales, English patent 1292, 1905; Boehme and Wolff, English patent 23,013, 1909. For an adulterated soap of this class cp. English patent 1292, 1905; cp. also Krüger, *Färber-Zeitung*, 1902, 289; *Chem. Zeit.*, 1908, 935; H. F. Slack, English patent 8934, 1913; J. Simons and Durkheim, German patent 309,574, 1916.

[8] Jaeckels, English patent 26,857, 1908.

Attempts are being made at present to make soap with the aid of *naphthenic acids*, which are recovered in the Russian oil industry from the "soda tar" obtained in the refining of petroleum fractions. As naphthenic acids alone yield a viscous or even liquid soap, they are sold as a "substitute" for fatty material under fancy names such as "saponaphtha"; they are stated to be used to some extent in the manufacture of low-class Russian soaps,[6] the chief component of which is coconut oil. The presence of naphthenic acids in a soap, unless declared, would, therefore, have to be looked upon as adulteration.[7] Their presence in a soap would betray itself by an extremely unpleasant smell of petroleum, by the deep green colour of their copper salts,[8] and by their low molecular weights, viz. about 215 (the theoretical number for $C_{13}H_{24}O_2$ is 212). The use of metallic salts of naphthenic acid in conjunction with naphthenic glycerides has been proposed as a substitute for india-rubber.[9]

The following is an analysis, due to *Charitschkoff*,[10] of a soap made from naphthenic acids, and sold as a "disinfectant" soap or "mineral" soap:—

Naphthenic acids	27·3	per cent.
Total alkali	18·3	„
Sodium carbonate	1·22	„
Water [10]	48·5	„
Impurities	4·4	„

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[1] See Vol. II. Chap. XIII. p. 35; cp. also German patent 157,737 (zinc peroxide); English patent 19,809, 1905; French patent 392,955 (Beiersdorf and Company); and English patent 16,823, 1908 (Wolffenstein); English patent 1150, 1909 (sodium peroxide and carbon tetrachloride). Gruner, German patents 167,793 (sodium peroxide), 190,140, 191,887, 193,738, 193,739, 197,376, 197,377.

[2] Giessler and Bauer, German patent 149,335; *Chem. Werke vorm. Dr. H. Byk*, English patent 7945, 1909; Hungarian patent applications C. 1874 and C. 1937; German patents 254,210; 258,393; Palanca and Co., Italian patent 341/135/112,472; A. Radisson, French patent 398,302; E. Herrmann, French patent 398,448; cp. also United States patent 941,158 (Mansolss and Rössler and Hasslacher, *Chem. Fabr.*).

[3] English patent 717, 1909 (Hollingworth).

[4] Fattinger, English patent 11,953, 1910.

[5] To this class would belong soaps containing sodium sulphide, *Chem. Werke in Freiburg i/B*, French patent 341,159; English patent 18,152, 1904; German patent 189,873; cp. also Diesser and Wohlrab, German patent 258,655. Such soaps are specially made for the use of workmen in white lead works.

[6] Cp. E. Pyhälä, *Petroleum*, 1908, 571; 1313. L. Mazet, *Les Matières grasses*, 1908, 1222.

[7] Cp. H. Breda, English patent 19,477, 1906; German patent 179,564; Bazin, French patent 399,212.

[8] The naphthenic acid has been proposed as a qualitative reagent for copper and cobalt, inasmuch as the metallic salts are soluble in ether, benzin, etc., yielding highly coloured liquids, Charitschkoff, *Chem. Zeit. Rep.*, 1910, 157; cp. also Lutschinnsky, *Chem. Zeit.*, 1911, 1204.

[9] Chercheffsky, German patent 228,858.

[10] *Chem. Zeit. Rep.*, 1907, 226. The original states: 28·48 per cent of water; this must be due to a printer's error.

Another analysis[1] of naphthenic soap (sold as "Miloin") gave the following results:—

Naphthenic acids	50·96 per cent
Total alkali, as NaOH	13·98 ,,
Combined alkali, as NaOH	9·30 ,,
Free sodium hydrate	1·85 ,,
Sodium carbonate	3·74 ,,
Naphthenic soda soap, anhydrous	56·07 ,,
Neutralisation value of the naphthenic acids	255 ,,
Mean molecular weight	219 ,,

The iodine value of naphthenic acids is given by *Charitschkoff* as 1·1.

Soaps of naphthenic acids require even more salt in the salting-out process than do the corresponding coconut oil and palm kernel oil soaps.[2]

Valuation and Analysis of Soap

In the foregoing lines the order of enumeration and classification of soaps within the two sections is chiefly based on the proportion of fatty acids which they contain. Hence in the valuation of soap, chemical analysis must play a prominent part, inasmuch as only thereby is it possible to ascertain the percentage of real soap, the amount of other constituents, and the presence of foreign substances. Whilst chemical analysis will thus be resorted to in the first instance, it must not be forgotten that a host of other factors, such as appearance, consistence, lathering properties, etc., play an important part in enabling one to arrive at a definite opinion as to the value of a soap. Not every soap is suitable for a given purpose, and much depends, *cæteris paribus*, on the nature of the fat stock which has been employed.

Stiepel[3] attempts to measure the lathering capacity of soap by dissolving in 100 c.c. of water an amount of soap corresponding to 0·6 grm. of fatty acids. This solution is placed in a flask of 2 litres capacity provided with a long graduated neck, on the top part of which is a bulb holding 50 c.c. The flask is well shaken for 30 seconds at a temperature of 17°-20° C. (or at 50°-55° C.) and inverted when, after standing for about three minutes, the amount of froth can be read off.

According to the standards laid down by the Government of New South Wales, soap must contain not less than 59 per cent of fatty acids plus rosin acids, not more than one-tenth of one per cent of free caustic alkali and not more than 3 per cent of sodium carbonate. If filling material be added, which must not exceed 10 per cent, the product must be labelled "soap mixture."

Hillyer[4] proposed to value a soap by determining the emulsifying power of the soap solution, on the assumption that this might form a measure of the cleansing power. As *Hillyer* himself agrees that this test in the form described by him does not supply an exact measure, the reader must be referred to the original paper. Tests of this kind would only have practical importance for establishments using large quantities of soap, such as laundries, woollen mills, etc. In these establishments the value of a given soap is ascertained by practical tests, the quantity of soap required to do a certain amount of work being actually determined on a large scale.

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[1] *Chem. Zeit. Rep.*, 1908, 610; cp. also Schwarz and Marcusson, *Chem. Revue*, 1908, 165; Bontoux, *Les Matières grasses*, 1911, 2156.

[2] Davidsohn, *Zeits. f. angew. Chem.*, 1914, 2.

[3] *Seifensieder Zeit.*, 1914, 347.

[4] *Journ. Amer. Chem. Soc.*, 1903, 1256. Cp. F G. Donnan, *Zeits. f. physik. Chem.*, 1899 31), 42; cp. also Bein, *Chem. Zeit.*, 1908, 236.

Shukoff and Schestakoff[1] also attempted to determine the washing power of soaps made from different oils and fats. According to their experiments the washing power of the soaps decreases in the following order :—Tallow, liquid vegetable oils and olein, coconut, palm kernel oils. These observers also state that the maximum cleansing effect is observed when the concentration of true soap in the solution is 0·2 to 0·4 per cent.

In the following lines the most reliable chemical methods (leaving out a number of proposed processes) applicable in the examination and valuation of commercial soaps will be described.[2] No attempt is made to indicate a complete course of analysis embracing the search for all substances that may possibly be present, as such a course would be of little practical use.

Sampling of Soap

Great care must be exercised in sampling soap in order to avoid serious errors in the determination of water. On exposure to the air, soap dries on the surface, and once a " skin " is formed the outer portions of a cake protect to some extent the inner portions from loss of water by evaporation. In the case of hard soap the sample for analysis should therefore be taken from the centre of the cake by cutting away all the outer portions ; to what extent this must be done will be gathered by inspecting a transverse section, this showing to what depth drying has taken place. The inside and outside give different proportions of fatty acids. Such devices as taking a sample by means of a cork-borer, or by cutting a transverse slice from a cake, in order to obtain an " average " sample, lead in most cases to erroneous results. This method of taking the inside of a bar will, of course, show, as nearly as possible, the percentage of fatty acids in the soap as it left the works. If, however, the soap is sold in bars of definite weight which have dried out considerably and the loss of weight to each bar has been taken into account, then the fatty acids must be determined in a transverse section. If the sample under examination be a freshly made soap (containing about 30 per cent of water), a fairly large portion should be weighed off rapidly, as the soap is apt to give up perceptible quantities of moisture to the dry atmosphere of the balance case. For the same reason the sample should not be sliced before weighing, except perhaps in the case of a milled toilet soap or of a thoroughly dried-out soap. The well-known contrivances for preventing loss of moisture during weighing must be resorted to, if highly watered soaps be under examination.

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[1] *Chem. Zeit.*, 1911, 1027.

[2] For the specifications of the various grades of commercial soaps, together with the methods of analysis recommended by the United States Bureau of Standards, see Circular No. 62, 1916, *Journ. Soc. Chem. Ind.*, 1917, 392.

Similar precautions must be taken in the case of soft soap. If a keg of potash soap is to be examined, the sample must be taken from the centre.

(*a*) *Determination of Fatty Matter and of Total Alkali*

The following is a rapid and, for the purposes of commercial analysis, sufficiently accurate process :—

Weigh off accurately 5 to 10 grms. of the sample (or 50 grms. on a balance sensitive to centigrammes), and dissolve in hot water in a beaker or porcelain basin by heating gently ; stir continually with a glass rod so as to prevent the soap from caking on to the bottom of the vessel. Add a few drops of methylorange, and run in gradually hydrochloric or dilute sulphuric acid (or dilute nitric acid if chlorides and sulphates are to be determined) until there is an excess of mineral acid. Heat with constant stirring until the separated fatty acids have melted into oily drops, add about 5 grms. (or 20 grms. for 50 grms. of soap) of dry beeswax or paraffin wax [1]—the paraffin wax should of course not give off volatile substances at 100° C.,—weighed accurately on a tared watch-glass (which is used afterwards for weighing the fatty matter), and heat again until the mixture of fatty matter and wax has collected on the top of the liquid as a clear, transparent oily layer, free from specks. Rinse off the glass rod with boiling water, heat until the fatty matter has again collected into one mass, remove the vessel from the source of heat, and allow the fatty layer to solidify by cooling. A white precipitate on the bottom of the beaker will indicate the presence of silicate or of " fillings " insoluble in mineral acids.

The solidified cake is then detached from the vessel by means of a platinum spatula, lifted out of the liquid, rinsed off with cold water, and placed on filter paper. Any small quantity of fatty substance adhering to the sides of the vessel is carefully scraped off and added to the cake. Dry the cake (by touching lightly with filter paper), place it on the watch-glass used before, bottom side upwards, allow to dry in a desiccator, and weigh. (For the control of works' operations, when 50 grms. should be used, it is sufficiently accurate to weigh immediately after drying with filter paper, taking care that no moisture remain in the cavities (if any) of the cake.) Should the cake contain any cavities (which only occurs when the fatty matter has not been heated properly), enclosing water and perhaps even mineral acid,[2] the fatty matter should be remelted in a basin over water, taken off after solidifying, and dried as described before.

From the weight thus found the weight of the wax is deducted, and the difference returned as **fatty matter.** If no closer examination is made, this is, as a rule, returned as **fatty acids.** This is, however, only correct if the absence of *neutral fat*, *wax*, and *unsaponifiable matter* has been proved, *rosin acids* being looked upon as so much fatty acids, unless their separate determination is desired.

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[1] The addition of wax may, of course, be omitted if it is known that the fatty matter will set to a solid cake on cooling.

[2] This can only occur if the operation has not been carried out carefully.

In case the sample of soap contains any foreign matter (such as fibre, potato starch, etc.), from which the fatty matter does not separate readily, it is best to extract with ether, and to determine the weight after evaporating off the solvent. In many cases the foreign matter can be separated from the soap by treating the sample with hot alcohol, in which the soap dissolves, and filtering off.

Any *soluble* fatty acids which are present in the soap pass to some extent into the acid liquor ; as a rule, they may be altogether neglected, except where coconut and palm-nut oil soaps are examined. In that case it is best to work with concentrated solutions, or, if convenient, to add common salt, which throws the bulk of the soluble acids out of the aqueous solution, so that the remainder may be mostly disregarded. If great accuracy be required the soap should be decomposed with mineral acid under ether or low-boiling petroleum ether, or a mixture of both solvents, so that the fatty matter is brought into ethereal solution. If petrol ether alone be used, water can be excluded easily, so that the drying of the fatty acids can be effected at low temperatures. A less accurate method is to titrate the aqueous solution with standard alkali until it is neutral to methylorange, then to add phenolphthalein and again to titrate with decinormal alkali. It is sufficiently accurate to calculate the alkali used in the second titration to caprylic acid, $C_8H_{16}O_2$, molecular weight 144, and to add the amount so found to the bulk of the fatty matter (cp. *Fendler and Frank* [1]).

Budde [2] proposes to precipitate the fatty acids by means of an excess of standardised copper sulphate solution. The precipitated copper salts are dried and weighed, the excess of copper being determined iodometrically. *E. Bosshard and F. Comte* [3] propose to connect the fatty acids into their lead salts and weigh them as such.

A very large number of processes purporting to introduce greater accuracy have been recommended by different chemists, but in the author's opinion they unnecessarily complicate the analysis, without offering any advantages. One of the simplest, due to *Schutte*,[4] which gives good results when known materials have been used, is to dissolve the soap in water, decompose a measured volume with acid and centrifuge it in a graduated tube, the volume of fatty acids being read off and calculated to percentage.[5]

If by subsequent examination the soap be found to be free from neutral fat, wax, and unsaponifiable matter (p. 365), the fatty matter is returned as **fatty acids.** If a complete analysis of the soap is desired these are calculated to fatty anhydrides. Since 100 parts of stearic acid, $C_{18}H_{36}O_2$, correspond to 96·83 parts of stearic anhydride, $(C_{18}H_{35}O)_2O$, and similarly 100 parts of palmitic acid, $C_{16}H_{32}O_2$, to 96·48 parts of palmitic anhydride, $(C_{16}H_{31}O)_2O$, and 100 parts of oleic acid, $C_{18}H_{34}O_2$, to 96·81 parts of oleic anhydride, $(C_{18}H_{33}O)_2O$, no appreciable error is committed if 3·25 per cent be deducted, or, what amounts to the same, if the percentage of fatty acids be multiplied by 0·9675. If the proportion of rosin acids in the soap be required, the fatty matter must be examined by *Twitchell's* method (Vol. I. Chap. X.) and the rosin acids calculated to the original soap (see below).

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[1] *Zeits. f. angew. Chem.*, 1909, 253.

[2] *Seifensieder Zeit.*, 1911, 418.

[3] *Helv. Chim. Acta.*, 1918 (1), 251.

[4] *Seifensieder Zeit.*, 1913, 551 ; cp. also Dominikiewicz, *Chem. Zeit.*, 1909, 728.

[5] H. F. Slack, *Pharm. Journ.*, 1915 (95), 696.

The more fatty acids a sample contains, the more actual soap is present. A comparison of the result of the analysis with the theoretical compositions given above will assist in the valuation of a soap. Any hard soap containing more than 64 per cent of fatty acids has either dried spontaneously on keeping, or has been dried artificially, as in the case of milled toilet soaps; hard soaps containing less than that amount have been reduced intentionally, and may contain an excess of water or alkali, or any of the many adulterants that are incorporated with soap.

The determination of the **total alkali** in a soap is conveniently combined with the determination of the fatty matter by using an accurately measured volume of standardised acid for decomposing the soap. The acid liquor is then filtered to remove traces of fatty acids, and the excess of acid is titrated back with standardised alkali (see below).

The alkali is calculated to caustic soda, Na_2O, in the case of hard soaps, and in the case of soft soaps to caustic potash, K_2O. Some hard soaps may contain small quantities of potash, but this may be, as a rule, disregarded. More frequently soft soaps contain notable proportions of soda. If a separate determination of soda and potash be required, the soap must be decomposed with hydrochloric acid, and the potash in the acid liquid estimated as potassium platinic chloride, in the usual manner. From the amount of potash so found, and from the quantity of acid required to neutralise the total alkali, the amount of caustic soda in the soap is calculated. Of course, any other method used in mineral analysis may be employed.

(*b*) *Combined Alkali, Free Caustic Alkali, and Alkaline Salts*

The total alkali is the sum of the several amounts of alkali present in the soap as (1) *alkali combined* with fatty (and rosin) acids, termed conveniently *combined alkali*; (2) *free caustic alkali*; (3) *alkali as carbonate,* or (and) *silicate,* or (and) *borate.*

1. *Combined Alkali* is usually found by difference, *i.e.* by subtracting the sum of the amounts of alkali obtained for (2) and (3) from the total alkali as determined above. It can, however, be found direct by titrating the alcoholic solution of the soap with normal acid (see below), using methylorange as an indicator after neutrality has been established to phenolphthalein. This may be done as a check, or in order to dis-

pense with the determination of the alkali present as carbonate, silicate, and borate (3), which obviously can then be found by difference.

2. *Free Caustic Alkali.*—A preliminary test is made by dropping an alcoholic solution of phenolphthalein on to a freshly cut surface of the soap. Pink coloration indicates the presence of free caustic soda (also of carbonate, silicate, and borate if the soap be moist). If the soap is dried out the alkaline salts do not redden the phenolphthalein. In order to separate free caustic alkali from any alkaline salts, a portion of the sample is dissolved in absolute alcohol and filtered. The alkaline salts remain on the filter, so that the alcoholic filtrate may now be titrated, using phenolphthalein as an indicator.

Free caustic alkali should be absent from well-made soaps, especially from toilet soaps. As a great deal of circumspection and experience is required so to "fit" a soap that it contains practically no free alkali, most of the ordinary commercial soaps will be found to contain an excess of free alkali. If this be small, the free caustic soda is mostly converted into carbonate, on exposure to the atmosphere, so that in many cases no free alkali will be found, especially if only the outer portions of a cake be tested. If, however, the excess of free caustic soda in a soap be large, as is notably the case in scouring soaps and in cheap toilet soaps made by the cold process, the detection of free alkali will offer no difficulty.

It should be borne in mind that under the term "free alkali" frequently all that alkali is understood which is not combined with fatty (or rosin) acids to form true soap, so that carbonate, silicate, and borate are included in "free alkali." I define here free alkali as free caustic alkali, thus differentiating it from the alkaline salts.

Free caustic alkali is determined quantitatively (*Hope*[1]) by dissolving 10 to 30 grms. of the sample in hot absolute alcohol in a flask, loosely corked in order to prevent absorption of moisture from the air. Highly watered soaps must be first dehydrated to some extent, whilst access of carbon dioxide is excluded. The hot solution is filtered rapidly, care being taken that no soap-jelly separates out on the filter; if the operation is carried out judiciously, a hot water funnel can be dispensed with.[2] The filter is washed with absolute alcohol, and the filtrate received in a narrow-mouthed flask. Phenolphthalein is added, and the solution is then titrated with decinormal hydrochloric acid. In some cases the alcoholic soap solution may exhibit an acid reaction to phenolphthalein. Acidity may be due to the soap containing an acid stearate (palmitate or oleate, cp. Vol. I. Chap. I.) owing to faulty "fitting," or to fatty acid having been added to "kill" an excess of alkali. The amount of decinormal alkali required to neutralise the solution is calculated to *free fatty acids,* in terms of oleic acid. Another although less accurate method is to precipitate a solution of the soap in 50 per cent alcohol with barium chloride. In this manner the fatty acids together with carbonic acid, silicic acid and boric acid are precipitated as barium salts which can be filtered off and the free caustic alkali titrated in the filtrate in the usual manner.[1] A method proposed by *F. H. Newington*,[2] which obviates the use of absolute alcohol, consists essentially in precipitating the soap from its aqueous solution by means of sodium sulphate and titrating the free caustic alkali with $\frac{1}{10}$th normal sulphuric acid, using a solution of silver-nitrate as the spot indicator.

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[1] *Chem. News,* 1881 (43), 219.

[2] Spaeth recommends to use a *Soxhlet* extractor (cp. *Journ. Soc. Chem. Ind.,* 1896, 139), but in my opinion this introduces an unnecessary complication.

3. The precipitate left on the filter contains *carbonate*, *silicate*, and *borate*, with which other insoluble substances, added as " fillers " (such as starch, talcum), as also colouring matters, may be admixed. (With regard to the *complete* examination of this precipitate see below.) To determine the alkali contained in the alkaline salts the precipitate on the filter is washed with cold water (see (*e*) 1), and the filtrate is titrated with standardised acid, using methylorange as an indicator. The acid used is calculated to Na_2O.

(*c*) *Determination of Water*

The direct determination of water in soaps is, as a rule, an unnecessary operation. In the case of genuine soaps it suffices for all practical purposes to calculate the fatty acids to anhydrides, and add their weight to the amounts of alkali in its various forms. The water is then found by difference. Soaps reaching the analyst's laboratory have, as a rule, lost more or less water by drying ; hence the direct determination of water in soaps does not afford a reliable means of valuation. For it must be remembered that ethereal oils (present even in many household soaps) volatilise with the water, as does alcohol (present in small quantities in some kinds of transparent soaps), and, to an appreciable extent, also glycerol (present in notable quantities in soaps made by the cold process, as also in some toilet soaps). Moreover, if a soap contains considerable proportions of free caustic soda, part of the loss will be compensated by the absorption of carbon dioxide from the atmosphere.

The direct determination of water is therefore only resorted to in exceptional cases. The soap is then cut into fine shavings, brought into a porcelain dish, and weighed with a glass rod, so that the skin which forms on drying and prevents the escape of water from the inner portions may be conveniently broken up from time to time. This is especially necessary in the case of highly watered soaps. *R. Hart*[3] recommends to distil off the water from the soap after the addition of an equal weight of commercial oleic acid and a quantity of xylene previously saturated with water.

For the purpose of valuing a sample of soap by chemical means the determinations described under (*a*) to (*c*) will suffice in most cases. Further tests embrace the examination of the fatty matter, and the detection and determination of other constituents of the sample.

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[1] Kling, Genin and Florentin, *Bull. Soc. chim.*, 1914, 200. Cp. also Bosshard and Huggenberg, *Zeits. f. angew. Chem.*, 1914, 11 ; and J. Russ, *Phys. Chem. Soc.*, 1916 (48), 411.

[2] *Journ. Soc. Chem. Ind.*, 1916, 95.

[3] *Journ. Ind. Eng. Chem.*, 1918 (10), 598.

(*d*) *Examination of the Fatty Matter* ("*Soap Stock*")

If no wax has been employed in the separation of the fatty matter, the latter may be used direct for the following tests. Otherwise a fresh quantity of fatty matter must be prepared; the cuttings of the soap are most conveniently used up for this purpose.

The fatty matter may contain, besides *fatty acids*—

1. Rosin acids.
2. Neutral fat.
3. Unsaponifiable matter.

1. **Rosin Acids.**—Rosin acids are detected qualitatively by the *Liebermann-Storch* reaction. For their quantitative estimation see Vol. I. Chap. X. For a method based on the solubility of the sodium soaps in acetone the original paper by *Leiste and Stiepel*[1] should be consulted. In the case of low-class soaps made from waste fats or their fatty acids there may occur oxidised fatty acids, as also in the case of soaps made from "black grease," fish stearine, etc. The fatty matter will in such cases reveal its presence by the dark colour. If the presence of oxidised fatty acids be suspected, their quantity is ascertained by separating the bulk of the fatty acids, which are soluble in petroleum ether, from the oxidised acids. A rapid method due to *V. Fortini*[2] is based on the insolubility of nitrated rosins in petroleum ether. The test is carried out as follows: 2 grms. of the mixed fatty and rosin acids are dissolved in 50 c.c. of petroleum ether in a separating funnel. A mixture consisting of 25 c.c. nitric acid, specific gravity 1·52, and 75 c.c. of nitric acid, specific gravity 1·48, is prepared, and 10 c.c. of this mixture, after the addition of a crystal of urea, are added drop by drop to the petroleum ether solution, followed by shaking. After being allowed to settle the acid layer is drawn off and the solution shaken with a further 5 c.c. of nitric acid. This is then drawn off and the petroleum ether washed first with nitric acid and finally with water until free from acid. It is then filtered and distilled off, the remaining fatty acids being weighed. It appears likely that this method will break down in the presence of highly unsaturated fatty acids.

2. **Neutral Fat.**—A well-made soap will but rarely contain unsaponified fat. If neutral fatty substances have been added to the finished soap, as in the case of "super-fatted" soaps (admixed with olive oil, etc., or in the case of certain toilet soaps, with wool wax), they will be obtained together with any unsaponifiable matter present, and must be separated from it subsequently.

The neutral fat *plus* unsaponifiable is isolated in a direct manner from the sample of soap by dissolving a weighed quantity in water or alcohol, adding standardised caustic potash to neutralise free fatty acids (if any), phenolphthalein being the indicator, and exhausting the soap solution as described Vol. I. Chap. VI.

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[1] *Seifensieder Zeit.*, 1913, 1233.

[2] *Annali Chim. Appl.*, 1918 (9), 102.

The residue from the ethereal solution consists of neutral fat *plus* unsaponifiable matter. The separation of the two constituents is effected by saponifying the mass, and again extracting with ether.

If unsaponifiable matter be absent, the total ether residue consists of neutral fat; otherwise the neutral fat is found by difference, or may be found in a direct manner by isolating the fatty acids and calculating their amount to glycerides.

A complication arises if the soap contain wool wax. If the presence of the latter be suspected, the ether residue should be saponified with dilute alcoholic potash on the water-bath, so as to obtain part of the wool wax as unsaponifiable matter, which can then be examined and identified.

3. **Unsaponifiable Matter.**—This is isolated and estimated together with neutral fat as described above. If no neutral fat has been found, the total ether residue consists of unsaponifiable matter. This is examined as described Vol. I. Chap. IX.

In addition to the substances mentioned in Vol. I. Chap. IX. the presence of vaseline, paraffin oil, oil of turpentine, tar oils, naphthalene, petroleum hydrocarbons, hydrocarbons from "distilled grease," etc., may be suspected.

Carnaüba wax, stated in some text-books as being usually admixed with soaps in order to render possible the incorporation of large proportions of paraffin oil, is not used in practice, as the same object can be attained by cheaper methods.

The examination of the FATTY ACIDS themselves, after separation from oxidised acids (if any), rosin acids, neutral fat, and unsaponifiable matter, with a view to determining the nature of the "stock," is a complicated problem, requiring systematic application of the methods described in the first volume of this work.

(*e*) *Substances insoluble in Alcohol*

The estimation of all those substances which are insoluble in alcohol is conveniently combined with the determination of free caustic alkali (see p. 362), by collecting the insoluble matter on a tared filter previously dried at 100° C., and weighing after drying at 100° C.

Good soaps yield but insignificant amounts of residue. Only transparent soaps manufactured by the "alcohol process" will be found absolutely free from insoluble matter.

The residue obtained on the filter may consist of—

1. Water-soluble substances, such as chloride, sulphate, carbonate, silicate, or borate of the alkalis.

2. Mineral substances insoluble in water, viz. colouring matters and "filling" and "weighting" substances.

3. Organic substances, especially starch, dextrin, or gelatin (carragheen mucilage, casein or vegetable meal).

1. **Water-soluble Substances.**—The residue on the filter is washed

with cold water so as not to dissolve any gelatin that may be present. Presence of silicate (if any) will have been noticed already in the determination of fatty matter when decomposing the soap by acid (see above under (*a*)). If the silica has not been estimated in the same portion in which the amount of fatty matter has been ascertained (provided no other water-insoluble substance be present), it can be determined at this stage by acidifying the filtrate with hydrochloric acid after the total alkali present in it has been determined by titration, see (*b*) 3, and evaporating to dryness in the usual manner. The filtrate from the separated silica may be tested for boric acid.

If boric acid be absent, the amount of carbonate *plus* silicate can be calculated from the alkali found by titration, the silica having been found direct by weighing. If boric acid be present and the proportion of borate be required, the water-soluble portion is best divided into three parts. In one portion the carbon dioxide is estimated, in a second portion the silica, and in the third the total alkali is determined by titration. Boric acid is determined in a direct manner, as in dry soap powders, by titration with alkali in the presence of glycerine.[1]

Chlorides and *sulphates* are best determined in aliquot portions of the acid liquor, obtained after separating off the fatty matter as described in (*a*). It should be remembered that for the present purposes nitric acid must be employed for decomposing the soap. A rapid method[2] for the determination of sodium chloride consists in weighing 5·85 grms. of soap which is dissolved in 150 c.c. of hot water. To the solution are added 25 c.c. of a 20 per cent solution of magnesium nitrate. The mixture is titrated without filtering with $\frac{1}{10}$th normal solution of silver nitrate, using potassium chromate as an indicator. If the above given proportions are used 1 c.c. of the silver solution equals 0·1 per cent of sodium chloride.

2. The **water-insoluble portion** is ignited, so as to burn off organic substances, and the residue is weighed. The ash is examined qualitatively and quantitatively in the usual manner.

3. **Organic Substances.**—The microscopical examination of the total residue insoluble in alcohol may furnish useful indications. Thus *starch* will be detected; the microscopical examination may be corroborated by testing with iodine. If the quantitative determination of starch be required, the alcohol-insoluble residue on the filter is washed with cold water to remove water-soluble substances and *dextrin*, and boiled with dilute sulphuric acid, replacing the water as it boils away in order to convert the starch into glucose. The liquid is then neutralised with barium carbonate, filtered, and the amount of glucose estimated by titration with *Fehling's* solution in the usual manner.

Dextrin has been washed out by cold water simultaneously with the soluble salts. The proportion of dextrin is estimated by precipitation with alcohol. This is done best in a small beaker, tared with a glass rod. The liquid is stirred vigorously, so that all the dextrin is made to adhere to the sides of the beaker. The aqueous liquid is then poured off, the dextrin washed with alcohol, and its amount determined by weighing the beaker after drying at 100° C.

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[1] Cp. Jacobi, *Seifensieder Zeit.*, 1910, 1230; also Poetschke, *ibid.*, 1914, 899.

[2] H. C. Bennet, *Journ. Ind. and Eng. Chem.*, 1921, 813.

Gelatin is dissolved by washing the alcohol-insoluble residue with hot water. The filtrate should be tested with tannic acid to corroborate the presence of gelatin.

(*f*) *Other Substances occurring in Soaps*

1. **Glycerol.**—The minute quantity of glycerol left in hard soaps, made by the "hot process," can only be determined accurately if a large quantity of soap be employed. The glycerol passes into the aqueous liquid on decomposing the soap with mineral acid, and is determined as described under estimation of glycerol in spent soap-lyes (see below). In the case of a soap made by the "cold process," about 5 per cent of glycerol will be found. The *absence* of glycerol from soft soaps will prove that fatty acids have been used as "stock."

Considerable quantities of glycerol are intermixed with certain toilet soaps made by the milling process. On account of its cosmetic properties such glycerol must be considered to be a valuable ingredient of these soaps. The glycerol is determined by dissolving the soap in water, separating the fatty matter by a mineral acid, and filtering off. The filtrate is neutralised with barium carbonate, and boiled down to the consistence of a syrup. The residue is then extracted with a mixture of three parts of 95 per cent alcohol and one part of ether, the alcoholic solution is filtered and evaporated on the water-bath to a small bulk, and finally dried under a desiccator. The glycerol in the crude glycerin thus prepared is determined by the acetin process (Vol. I. Chap. VI.).

If sugar be present in a soap conjointly with glycerol, as in cheap transparent soaps, the sugar must be first removed (cp. below).

2. **Sugar** is found to a considerable extent (up to 25 per cent) in cheap transparent soaps. The determination of the saccharose is best effected by boiling the filtrate (or a measured portion of it) obtained in (*a*), with dilute sulphuric acid to invert the sugar *completely*, rendering alkaline, and heating with *Fehling's* solution after previous dilution so as to prevent oxidation of glycerol. The separated cuprous oxide is estimated in the usual manner and calculated to saccharose. If a considerable quantity of sugar be present, it may be determined polarimetrically.

If glycerol and sugar be present conjointly, separation is effected, according to *Donath and Mayrhofer*,[1] by adding to the solution sufficient slaked lime to combine with the sugar present, admixing an equal quantity of washed and ignited sand, then boiling down to the consistence of a syrup, pulverising the residue after cooling, and exhausting in a corked flask with 80-100 c.c. of a mixture of equal volumes of alcohol and ether. The solution will then contain the glycerol (free from sugar), and this may be estimated as described under 1.

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[1] *Zeits. f. analyt. Chem.*, xx. 383.

3. **Carbolic Acid.**—The determination of "carbolic acid" (phenol and cresols) in carbolic soaps [1] is carried out with sufficient accuracy by the following method (*Lewkowitsch*) :—

Weigh off a somewhat large amount of the sample, about 100 grms., dissolve in hot water and add sufficient caustic soda to render the solution strongly alkaline. Then throw up the soap with common salt, filter off the curdy soap, and wash it with saturated brine. Boil down the solution which contains the phenol and cresols as sodium carbolate and cresylates, and precipitate any retained soap in the same manner. Filter again, boil down to a small bulk, and transfer the solution to a stoppered graduated cylinder of 50 or 100 c.c. capacity, add sufficient salt so that some remains undissolved, and acidify with sulphuric acid. The volume of the separated phenols is then read off and the number of c.c. taken as so many grammes.

Rapp [2] mixes 20 c.c. of cresol soap with 40 c.c. of glycerin and distils over 30 c.c. into a graduated cylinder, the temperature being kept below 280° C. The distillate is shaken with an equal volume of 66 per cent sulphuric acid, and after allowing to stand the volume of the cresol is read off. The soap solution remaining in the flask is decomposed with an excess of standard sulphuric acid when the fatty acids and alkali may be determined in the usual manner.

If greater accuracy be required, as is especially the case in soaps made with addition of pure carbolic acid—phenol—the separated "carbolic acid" is brought into ethereal solution and recovered after distilling off the solvent. The phenol and cresols may then be determined by *Koppeschaar's* method.[3] In the case of soaps made with crystals of phenol the last-named method should be applied on account of the considerable solubility of phenol in a salt solution. As a rule much smaller quantities of soap will suffice for the analysis.

4. **Alcohol.**—The determination of traces of alcohol left in transparent soap made by the alcohol process will be but rarely required. In the case of soaps with which considerable amounts of alcohol are incorporated [4] the alcohol is determined by distilling a weighed quantity of soap in a current of steam. If frothing cannot thus be prevented, a weighed quantity of soap is decomposed with sulphuric acid, the fatty acids are separated off by filtration, and the filtrate is distilled. From the specific gravity of the first 50 c.c. of the distillate and, if need be, from that of a second fraction, the amount of alcohol can be readily found.

5. **Formaldehyde.**—Formaldehyde which has been added to medicated soaps (cp. p. 352) may be determined by the following method

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[1] With regard to the bactericidal action of carbolic acid, cp. Rapp, *Apotheker Zeit.*, 1908, 737.

[2] *Apotheker Zeit.*, 1909, No. 70.

[3] J. Deiter, *Veröff. Militär. Sanitätsw. Med. Abt. d. Preuss. Kriegsminist.*, 1908, 73. The objections raised against the correctness of Koppeschaar's method by Lloyd (*Journ. Amer. Chem. Soc.*, 1905 (27), 16) have been shown to be groundless by S. C. J. Olivier, *Rec. des Trav. Chim. d. Pays-Bas*, 1909, 354. Cp. also Autenrieth and Beuttel; Redman, Weith and Brock, *Journ. Ind. Eng. Chem.*, 1913, 389; and W. Versfeld, *Analyst*, 1915, 281.

[4] Cp. R. Adam, English patent 2343, 1906 (Falck); German patent 149,793 (Wolff).

(*Allemann* [1]): 50 c.c. of the soap solution are diluted with about 200 c.c. of water. A slight excess of sulphuric acid is added, followed by barium chloride solution, and the whole diluted to 500 c.c. To 5 c.c. of the filtrate 40 c.c. of $\frac{1}{10}$ normal iodine solution is added, and a concentrated solution of caustic soda added drop by drop until the colour changes to bright yellow. The mixture is then allowed to stand for ten minutes, acidified with sulphuric acid and the excess of iodine titrated with sodium thiosulphate solution. Free oxygen due to the presence of per salts may be determined by the methods of *Archbutt* [2] *and Grossmann.*[3]

Saponins may be approximately determined by decomposing the soap with sulphuric acid and removing the fatty acids by means of ether. The acid liquid, after neutralisation with caustic soda, is evaporated to dryness and the residue extracted in a Soxhlet with absolute alcohol. The alcoholic solution contains the saponin together with any glycerin which may have been present in the soap. The bulk of the alcohol is distilled off and the saponin precipitated with a solution of barium hydrate. The precipitate is washed with the barium hydrate solution to remove the last traces of glycerin. It is then suspended in water and decomposed by a current of carbon dioxide. The aqueous solution contains the saponin, and after filtering off the insoluble barium carbonate it is evaporated to dryness and the residue weighed.

For the determination of active oxygen in soap powders, due to the presence of per salts (perborates, etc.), the following method may be employed: 1 grm. of the dry soap is weighed off and dissolved in 200 c.c. of water, 10 c.c. of sulphuric acid (1 : 2) are added, followed by the addition of an excess of a standardised solution of ferrous ammonium sulphate. The mixture is boiled for half an hour while a current of carbon dioxide is passed through. After allowing the solution to cool in a current of the gas, the excess of iron salt is titrated with decinormal potassium permanganate solution.[4]

6. **Colouring matters** in soaps cannot be considered as illegitimate admixtures, as coloured soaps are demanded in commerce. Provided the colouring matter be harmless, no objection can be raised. The analyst will, therefore, at most, only be required to state whether certain colouring matters contain poisonous metals or not.

7. **Ethereal oils** in soaps have almost become a necessary ingredient, even in better class household soaps. Their quantity will naturally be very small, and need not, as a rule, occupy the attention of the analyst.

Special methods must be worked out in each individual case for the detection, and, if need be, for the estimation of other substances put into soap, such as mercuric iodide,[1] or zinc peroxide,[2] or bismuth,[3] or formalin in antiseptic soaps.

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[1] *Zeits. f. analyt. Chem.*, 1910, 265.

[2] *Analyst*, 1895, 3.

[3] *Chem. Zeit.*, 1905, 137. Cp. also Pfyl, *Arb. a. d. Kais. Gesundheitsamte*, 1909, xxx. 87; Bosshard and Zwicky, *Zeits. f. angew. Chem.*, 1910, 1153.

[4] Wittels and Welwart. Cp. also Farrer, *Journ. Soc. Dyers and Colourists*, 1910, 81.

It is impossible to obtain reliable statistical data as to the production of soap in this country. A careful estimate made by the author would show that the quantity of hard soaps (toilet, laundry, household, and textile soaps) produced amounts to over 400,000 tons per annum. To this must be added about 1000 tons of soap powders per week.

Most of the soap is consumed at home; the quantities exported (see p. 11) represent therefore a small fraction of the total production.

With regard to *soft soap* it is still more difficult to give reliable data. A fairly accurate estimate would place the total make per annum for England and Ireland at 10,000 tons, and for Scotland at approximately 8000 tons per annum.

According to the Census of the United States for 1905 and 1910, the quantity of materials used in the manufacture of soap and the quantities and values of the products obtained in those years were as follows:—

	1905.	1910.	1905	1910.
	Lbs.	Lbs.	Value Dollars.	Value Dollars.
Materials used, total cost	..	..	43,625,608	72,179,418
Tallow, grease, etc.	475,618,277	413,969,787	19,723,311	23,341,905
Coconut and palm kernel oils	62,181,501	11,856,337 gals	2,692,034	5,875,294
Cotton seed oil	120,811,654	24,221,712 gals.	..	9,718,988
Palm oil	4,090,359	..	..	..
Olive oil	5,486,471	..	..	..
Castor oil	757,216	..	..	..
Turkey-red oil, distilled and saponified	4,419,827	..	..	..
Other oils	8,669,524	..	..	..
Rosin	168,107,246	207,296,447	..	4,362,412
"Foots"	59,761,740	94,050,892	..	2,453,609
	909,903,815 lbs. 406,207 (long) tons.			
Petroleum products, gallons	4,277,289	..	218,798	..
Caustic soda, tons	71,551	52,172	..	2,212,232
Soda ash, tons	53,777	121,016	..	2,281,787
"Mineral fillers," lbs.	31,075,233	..	238,393	21,933,191
All other materials	..	..	..	..
Products.[4] total value	..	..	68,274,700	111,357,777
Tallow soap	846,753,798	859,297,507	32,610,850	88,550,803
Oleine soap	29,363,376	32,832,647	1,363,636	..
"Foots" soap	85,000,133	151,063,102	3,090,312	..
Toilet soaps, including medicated, shaving, and other special soaps	130,225,417	93,823,149	9,607,276	..
Powdered soaps	120,624,968	275,745,585	4,358,682	..
All other kinds	143,390,957	323,978,476	6,097,670	..
Soft soap	33,613,416	44,052,615	667,064	943,676
Special soap articles	..	..	554,881	731,823
	1,388,972,065 620,077 (long) tons.		126,625,071	
Glycerin	27,660,661	39,689,300	2,958,105	5,713,558
All other products	..	..	7,216,154	15,417,890

The approximate consumption of soap per head of population is given in the following table due to *Krebitz*:—

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[1] Cp. A. Siedell, *Journ. Amer. Chem. Soc.*, 1906, 73.

[2] Cp. German patent 157,737.

[3] English patent 23,111, 1909 (E. Weyner).

[4] Products consumed in establishments where produced were: Turkey-red oil, 1,149,346 galls.; tallow, 10,613,271 lbs.; cotton seed oil, 920,410 galls.; caustic lye, 30° B., 9,568,532 galls.; sodium silicate, 1,597,886 lbs.; glycerin, 3,433,389 lbs.; framed soap, 114,452,424 lbs.

Russia	2·7-3·9	lbs.
Roumania	4·8	,,
Denmark	8·8	,,
Germany	8·0-10·0	,,
Norway	11·0	,,
Italy	11·6	,,
Sweden	13·2	,,
Belgium	13·2-14·9	,,
Holland	13·2-15·4	,,
Switzerland	13·2-15·4	,,
United States	15·0	,,
France	17·6	,,

The amount of soft soap made in the United States of America in 1909 was about 44 million pounds.

For other countries not even approximate data are available; but the consumption of soap reckoned per head of population is certainly much smaller in other countries than in this country and in the United States of America. France in 1898 has produced 300,000 tons of soap of which only 30,000 tons were *savon bleu pâle et bleu vif.* Marseilles produced 146,000 tons.

(2) SALTS OF THE ALKALINE EARTHS AND HEAVY METALS—WATER-INSOLUBLE SOAPS—METALLIC SOAPS

The insoluble soaps of the individual fatty acids as far as they have hitherto been obtained in a state of purity are described in Vol. I. Chapter III.

The soaps to be considered here are prepared by double decomposition of the alkali soaps with aqueous solutions of salts of the alkaline earths or metals, or by heating the free fatty acids with the oxides or carbonates of the metals.[1]

These soaps are employed in the arts for the most varied purposes. Their property of dissolving, to a considerable extent, in petroleum ether, heavier petroleum hydrocarbons, coal-tar oils, naphtha, oil of turpentine, carbolic acid,[2] and fatty oils [3] facilitates their application in the arts. The solubility of the soaps in the solvents named is increased by the presence of free fatty acids.[4]

Fay and Hamilton [5] state that the stearates and oleates of calcium iron, aluminium, zinc, copper, and lead are insoluble in cold linseed oil, turpentine and petroleum, but dissolve to a clear solution in the hot.

Magnesium Oleate.—A solution of this salt in petroleum ether is added to the organic solvents employed in the process of dry-cleaning silk goods, to prevent spontaneous conflagration when the silk goods are taken out of the solvent (as the magnesium oleate increases the conductivity of the solvent to such an extent that generation of electric sparks is prevented).

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[1] With regard to the metallic salts of naphthenic acids, see Pyhälä, *Petroleum*, 1908, 1313.

[2] German patent 148,794 (Raupenstrauch).

[3] The solubilities of the metallic soaps of linseed oil have been studied by Vulté and Gibson, *Journ. Amer. Chem. Soc.*, 1902, 215. It may be added that calcium "linoleate" (*i.e.* the calcium salts from the mixed fatty acids of linseed oil) is soluble in alcohol.

[4] For calcium salts of substituted fatty acids cp. p. 310.

[5] *VIII. International Congr. of Applied Chem.*, 1912, vol. xi., section v. d. p. 11.

This salt is sold on the Continent under the name "antibenzinpyrin" or "richteröl." It may, however, be added that the above-mentioned dry-cleaning soaps (see p. 355) alone are capable of preventing spontaneous ignition through electrical sparks.[1] The magnesium salt of dibromobehenic acid is used as a substitute for potassium bromide.

Strontium Soaps.—The strontium salt of a dibromobehenic acid is used in pharmaceutical practice as a substitute for potassium bromide.

Lime soaps are extensively employed in the manufacture of solid lubricants (see above) and, together with magnesium and aluminium soaps, for waterproofing textile goods.[2]

Aluminium soaps enter into many compositions for waterproofing textile goods and papers, for preparing substitutes for leather, celluloid, india-rubber substitutes for insulating purposes, etc.[3] A solution of aluminium oleate in benzene is sold as crystal or paper varnish. Aluminium oleate especially is used as an "oil thickener" (see above, p. 89).

Lead and **manganese soaps** are used as "driers" in the manufacture of boiled oils and varnishes (cp. p. 146).[4]

Lead plaster consists chiefly of lead oleate. Lead plaster prepared from oleic acid is completely soluble in ether, whereas plasters made from natural oils and fats yield an ether-insoluble residue consisting of the lead salts of the saturated fatty acids.

Zinc,[5] **iron, nickel, cobalt,** and **chromium soaps** are employed in the manufacture of coloured varnishes, as also for waterproofing leather, canvas, etc. **Copper** and **mercury soaps** are used in the production of anti-fouling preparations, especially in the manufacture of paints for ships' bottoms,[6] and added to ordinary soda soaps as antiseptics. Copper soap in colloidal form, prepared by mixing equal volumes of a 1 per cent solution of copper sulphate with a 4 per cent solution of a neutral soap, is used as a fungicide.[7] The metallic salts of naphthenic acids have also been prepared.[8]

In this class of soaps must be also included the **metallic rosinates.**[9]

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[1] Cp. Göhring, *Verein zur Beförderung des Gewerbefleisses*, February 1908.

[2] For the solubility of calcium soap in ammonium citrate cp. Justin Müller, *Chem. Zeit.*, 1904, 1149. Cp. also W. Haupt, *Zeits. f. angew. Chem.*, 1914 (27), 535; and J. Zink and R. Liere, *ibid.*, 1915 (28), 229.

[3] Cp. Thornton and Rothwell, English patent 4237, 1899; German patent 117,878; E. Agostini, French patent 361,772. Cp. also German patents 158,911 (C. O. Snavely), 190,817 (R. Köster); German patent application 13,559, 1909.

[4] For their use in the manufacture of camphene from pinene hydrochloride cp. English patent 19,960, 1906.

[5] Cp. French patent 332,788 (Bonneville et Cie); French patent 368,755 (Lecesne); German patent 194,726 (A. Plöger).

[6] Nördlinger (German patent 168,611) claims the metal salts of the volatile acids from acetic acid up to capric acid as admixtures to heavy tar-oil for impregnating, preserving, and disinfecting.

[7] Vermorel and Dantony, *Compt. rend.*, 1911 (152), 1263.

[8] Ubbelohde, German patent 261,070.

[9] Pardeller, *Seifensieder Zeit.*, 1909, 1337.

Lime rosinate is employed in the manufacture of solid lubricants, and aluminium rosinate[1] as a size for paper and for waterproofing materials.[2] Solutions of manganese rosinate and lead rosinate in warm linseed oil are used as liquid driers (cp. p. 147). Copper rosinate, like the copper salts of fatty acids, is used as a rust preventative and for painting ships' bottoms. Cobalt and gold rosinates are easily soluble in lavender oil; the solutions are used for painting on porcelain, when, on "burning" the painted porcelain, cobalt oxide and gold respectively remain behind. With regard to zinc rosinate see Chapter XVI., "Waste Waxes."

The metallic rosinates dissolve more readily in light coal-tar hydrocarbons than in petroleum ether.[3] The dissolution of metallic rosinates in coal-tar naphtha is assisted by dissolving in the naphtha a quantity of rosin equal in amount to that existing in the rosinates. (This holds especially good of mercury rosinate.) By this means any free hydrate or carbonate of the metallic base is neutralised.[4]

In the analytical examination, the water-insoluble soaps are decomposed by means of a suitable mineral acid (hydrochloric, nitric, sulphuric), when the fatty acids are obtained as an oily layer, or if the salts be decomposed under ether (which in many cases is the most advisable course) in ethereal solution, and the metal passes into the acid solution. Both the fatty acids and the acid liquor are then examined in the usual way.

IV. GLYCERIN MANUFACTURE

Whereas the chemically pure substance described in Vol. I. Chapter III. is termed "glycerol," those commercial products which contain glycerol in a more or less pure state are best comprised under the name "glycerin."

It has been pointed out already that glycerin is a by-product of the stearine-candle and soap industries. It is obtained in dilute aqueous solutions, which contain various impurities, the nature and quantity of which depend on the manufacturing processes. The purest raw material results from saponification by means of lime in open vessels (p. 220 and p. 339); hardly inferior to this is the glycerin obtained by "autoclaving" (p. 221 and p. 304). Less pure is the raw material recovered from the acid saponification processes (p. 237), *Twitchell's* process (p. 305), and the "ferment process" (p. 306). The crude glycerin obtained from soap lyes, notwithstanding its high proportion of inorganic salts, may surpass in quality (*i.e.* as regards the amount of organic impurities), the crude material from the last-named processes, but if fats and oils of low quality have been saponified by means of black-ash lyes it may be still more impure. Modern processes of refining have, however, overcome a number of difficulties caused by the various impurities, so that, *e.g.* chemically pure glycerin from good soap lyes cannot be distinguished from glycerins obtained by lime saponification. Crude glycerins vary in quality in accordance with the care exercised in the manufacture. Crude glycerins obtained from the acid saponification, the *Twitchell*, and the ferment processes, retain very tenaciously some organic impurities which hitherto seem to have defied all attempts to remove them, as the writer has ascertained in the case of a number of " chemically pure " glycerins originating from these processes.

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[1] Cp. German patent 118,307 (Peniakoff).

[2] Huwart, *Travaux de la Station de Recherches relatives à la pêche maritime à Ostende*, 1908, 30.

[3] The solution of metallic rosinates in coal-tar hydrocarbons may be diluted with light petroleum spirit, which assists in the drying of the rosinates. Truchot, *Journ. Soc. Chem. Ind.*, 1897, 449; cp. also Bottler, *Chem. Revue*, 1910, 292.

[4] With regard to mixed fatty acid salts and rosinates cp. French patent 385,062.

The several commercial **crude glycerins** are obtained by concentrating the aqueous solutions of glycerol after they have been subjected to suitable purification.

1. CRUDE GLYCERIN

The composition of commercial crude glycerins varies considerably with the process of saponification from which they originate. Up to the appearance on the market of crude glycerins from the *Twitchell* and the ferment processes, the following three commercial qualities were distinguished: Crude saponification glycerin, crude distillation glycerin, and soap-lye (soap crude) glycerin. The crude glycerins from the *Twitchell* and the ferment processes are offered in commerce as " saponification glycerin," but as this denomination would appear to clothe them with the attributes of a higher quality than they actually represent, the author considers them separately under the description of " *Twitchell* crude glycerin " and " Fermentation crude glycerin."

(1) Crude Saponification Glycerin

This glycerin represents the best quality of the crude glycerins. It is obtained from the " sweet water " (" *petites eaux de stéarinerie* ") of the autoclave processes, and as a by-product in the process of soap-making by double decomposition.[1]

According to the amount of water charged into the autoclave, and to the quantity of steam sent into the autoclave during the saponification process, the proportion of glycerin in the " sweet waters " varies from 6 to 16 per cent. The metallic oxides contained in the " sweet waters " are neutralised, and the filtered solution is concentrated by means of steam, either in a Wetzel pan (shown in Fig. 23), or, as is done in modern works, in a vacuum evaporator of a type identical with those shown in Figs. 24-27. According to the quantity of salts which separate when the bulk of water has been driven off, a vacuum evaporator either of the type A or type B, Fig. 27, is used. The evaporation is carried on until the crude glycerin contains about 85-90 per cent of glycerol. Its specific gravity is then from 1·240 to 1·242, corresponding to the commercial brand of "28° Bé. saponification crude" or "candle crude" glycerin. The colour of this glycerin varies from yellow to dark brown; its taste is sweet. With basic lead acetate it gives but a slight precipitate. By refining this crude glycerin with charcoal, a "refined" glycerin (used for a number of commercial purposes) is obtained. This crude glycerin contains up to 0·3 per cent of ash,[1] chiefly calcium (or magnesium or zinc) sulphate, and small quantities of organic impurities.

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[1] Vogt, Belgian patent 241,178, 1911; French patent 437,414. Joseph Kellner claims (German patent 208,806) the working up of the glycerin waters resulting from the treatment of the fatty acid layer (see p. 226) with dilute acid with a view to recovering the bases, as also the glycerin, contained therein. Of course these acid waters have never been wasted as the patentee appears to assume.

The valuation of this crude glycerin is based on the determination of the pure glycerol, the ash, and the organic impurities. The taste and smell should not be objectionable.

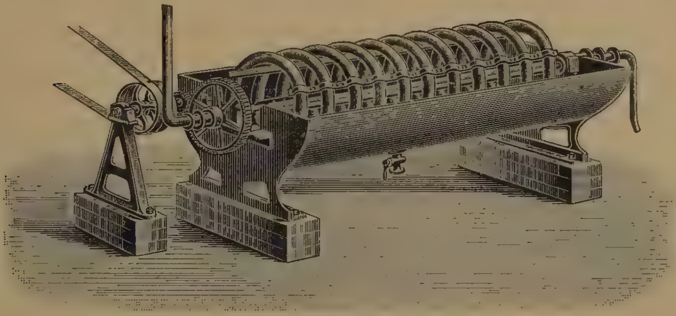

Fig. 23.—Wetzel Pan.

The percentage of *glycerol* is best ascertained by the acetin process. The oxidation methods, especially the bichromate method, are apt to lead to too high results (cp. Vol. I. Chap. VI.), especially if the glycerin contain any organic impurities which are not removable by the method of purification described below. Hence, although in some cases the acetin method and the bichromate method may lead to practically identical results, in most cases the determination by the bichromate method gives too high numbers, as is shown by the following table[2]:—

Comparison of the Acetin and Bichromate Methods (Lewkowitsch)

Saponification Crudo.	Acetin Method. Per cent.	Bichromate Method (purified with Copper Sulphate). Per cent.
1	89·91 ; 90·75 ; 90·43	93·68 ; 94·21 ; 94·71 ; 94·90
2	90·69 ; 90·74	92·70 ; 93·08
3	94·02 ; 94·12	97·21 ; 97·94
4	85·23 ; 85·42	86·72 ; 86·41

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[1] Glycerin obtained from bone fats extracted by means of carbon tetrachloride is stated to contain exceedingly high proportions of ash, even if the fatty material was carefully purified, previous to being autoclaved (*Seifensieder Zeit.*, 1907, 1210).

[2] Lewkowitsch, *Analyst*, 1903, 104.

The *ash* is determined by heating a few grammes of the sample in a platinum dish, and weighing the residue obtained on incineration.

The *organic impurities* may either consist of fatty acids which have not been completely removed, or of other organic substances, the nature of which has not yet been defined. Fatty acids are detected by diluting one part of crude glycerin with three parts of water, and adding strong hydrochloric acid. A turbidity points to the presence of fatty acids. The organic impurities are determined quantitatively by allowing a few grammes to evaporate slowly at 160° C. The residue is then weighed, and the weight of the ash found on incineration is deducted (cp. p. 388). The amount of organic residue gives a fair indication as to the care with which the glycerin has been manufactured. As a rule the quantity of organic impurities lies below 1 per cent.

The test for *arsenic* (see below) completes the chemical examination of the crude glycerin.

The "sweet water" obtained in the process of soap-making by double decomposition is treated in the same manner as is described above, and yields a good saponification crude, which is equal in quality to a "candle crude," provided that the original fatty matter was of good quality. As this process, however, is used in small works only, where chiefly low-quality greases are worked up, the crude glycerin obtained therefrom is high in ash, and is apt to contain a considerable amount of organic impurities, so that such crude glycerin is liable to ferment when stored; indeed, within the author's experience such crude glycerins did ferment. Samples of crude glycerin of this description examined by the author gave the following results:—

Specific Gravity . .	1·2527	1·2464
Ash	5·008 per cent	1·773 per cent.
Glycerol	77·1 ,,	84·3[1] ,,

The fact that this crude glycerin fermented would show that the organic substances in low-class greases are not destroyed by treatment with lime. By fermentation trimethyleneglycol is formed.

(2) CRUDE DISTILLATION GLYCERIN

This glycerin is recovered from the acid waters resulting in the acid saponification processes, and is termed in commerce *crude distillation glycerin*, for the reason that the fatty acids obtained by this process must be distilled to yield candle material. The dilute glycerin waters are worked up in the same manner as is described under (1), but owing to the large amount of sulphuric acid used in the process, a considerable amount of salts remains in solution after neutralisation of the mineral acid with lime. With the progress of concentration, especially when the crude glycerin approaches the specific gravity 1·240, sulphate of lime (which is no longer held in solution) drops out and is deposited on the heating surface of the evaporating apparatus in the form of a hard crust, which rapidly diminishes the evaporative power of the steam unless the calcium sulphate is removed. Hence, ordinary tube evaporators, such as are represented by vessel B in Fig. 27, are useless for concentrating the dilute solutions, and a type of evaporator must be employed which permits the heating surface to be continuously scraped so as to be kept clean and free from deposit. Such an evaporator is shown in Fig. 24, the inner construction of which is exemplified by the Figs. 25 and 26.

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[1] This number was obtained by the acetin method; as the crude glycerin contained trimethyleneglycol, the proportion of true glycerol must have been lower.

The finished crude glycerin contains considerable proportions of calcium sulphate, the solvent power of glycerol for calcium sulphate (Vol. I. Chap. III.) being apparently increased by the organic impurities which the crude glycerin retains. The ash of crude "distillation glycerin," therefore, amounts to as much as 2 and even 3·5 per cent. Also the amount of organic impurities is greater than in crude "saponification glycerin"; it may rise to even 2 per cent, the amount depending on the lack of care exercised in the manufacture. The colour of this crude glycerin is usually pale yellow; its taste is sharp and astringent, and it emits an unpleasant smell when rubbed between the hands. A voluminous precipitate is obtained with basic lead acetate; on addition of hydrochloric acid a turbidity appears, due to the presence of fatty acids.

This crude glycerin has the same specific gravity as has saponification glycerin, viz. 1·240-1·242, and contains, as a rule, from 84 to 86 per cent of glycerol. It is known in commerce as "distillation glycerin, 28° Bé."

The glycerol in this glycerin should be determined by the acetin process and not by the bichromate method. The differences in the percentage, as obtained by the two methods, is greater than in the case of saponification crude, owing to the larger amount of organic impurities. This is specially shown by a few examples reproduced in the following table (*Lewkowitsch* [1]):—

Comparison of the Acetin and Bichromate Methods (*Lewkowitsch*)

Crude Distillation Glycerin.	Acetin Method. Per cent.	Bichromate Method (purified with Copper Sulphate). Per cent.
1	86·26; 86·16; 86·22	89·70; 89·22
2	83·51; 83·68	89·44; 89·73
3	83·1; 82·98	83·9; 83·56; 83·52

The ash is determined by the method described above (p. 376). The organic impurities are best determined by the International Standard Method. Arsenic is detected as described below.

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[1] *Analyst*, 1903, 106.

(3) TWITCHELL CRUDE GLYCERIN

This crude glycerin is obtained from the acid water resulting in *Twitchell's* saponification process (cp. p. 305). The glycerin waters are treated with lime, or barium hydrate or barium carbonate, so as to precipitate the dissolved sulphuric acid as completely as possible. The purified liquors are concentrated up to a specific gravity of about 1·24 or more in the same manner as described above. The quality of this crude varies considerably with the quality of the fatty material from which it is made. If the raw material is of good quality, the glycerin is fairly good; but even in that case, owing to the higher amount of ash it contains, and owing to its unpleasant taste, it is valued at a somewhat lower price than crude candle glycerin. As an example may be given the analysis of a crude glycerin of this description examined by the author:—

Specific gravity	1·2390
Glycerol	84·8 per cent.
Ash	0·52 ,,

In candle works this process is mostly applied to low-class fats, such as "greases" (Chap. XVI.), and even to "garbage fats" (Chap. XVI.), as it works most profitably with low-class material containing high proportions of free fatty acids. Hence the glycerin obtained from such low-class material contains so considerable an amount of organic impurities that it cannot be worked up by itself, not even for the production of dynamite glycerin. Each special make of such glycerin is valued on the basis of the impurities it contains. Thus a commercial sample examined by the author may be given here:—

Specific gravity	1·2415
Ash per cent	0·48
Organic impurities per cent	1·879
Glycerol per cent	87·22

For the influence of the "*Twitchell* reagent" on the amount of organic residue, the reader must be referred to the papers by *Cocks and Salway*.[1]

(4) FERMENTATION CRUDE GLYCERIN

The sweet water from the fermentation process is rich in albuminoids and other organic impurities. It must, therefore, in addition to the usual treatment,[2] be filtered over char, which retains the bulk of the albuminoids and other organic impurities; nevertheless a certain amount remains in the glycerin, and consequently the finished crude is not only dark in colour, but has also a very unpleasant smell and taste, even if made from good raw material (refined cotton seed oil, refined linseed oil), and from the "ferment," as described above. In the infancy of this process the crude glycerin obtained was practically unusable. Thus, a sample examined by the author contained above 2·5 per cent of ash, and the amount of organic residue exceeded 3 per cent. Owing to the improvements made (cp. p. 308), these amounts have been considerably reduced, as is shown by the following analysis carried out in the author's laboratory with a crude glycerin made from refined seed oils.

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[1] *Journ. Soc. Chem. Ind.*, 1918, 123 T, 127 T, 158 T.

[2] The poisonous ricine (Vol. II. p. 404) is stated to be removed completely by precipitation with lime. *Atti del VI. Congresso Internazionale Roma*, 1907.

Specific gravity	1·2369
Ash	0·49 per cent.
Organic impurities (albuminoids, etc.)	1·54 ,,

(5) SOAP-LYE GLYCERIN, SOAP CRUDE GLYCERIN

The lyes obtained in the soap-making process by boiling glycerides in an open pan contain practically all the glycerol which the natural oils and fats employed are capable of yielding. According to the manner in which the " changes " of soap lyes are worked up, the spent lyes may contain from 5 to 8 per cent of pure glycerol. Besides glycerol, the spent soap lyes hold in solution the common salt used in " cutting " the soap, and also small amounts of free caustic soda, sodium carbonate, soap, and organic impurities.

The specific gravities of the spent lyes vary, as a rule, from 1·08 to 1·14, according to the amount of salt dissolved in them.

The value of spent soap lyes depends on their percentage of glycerol, and on their comparative freedom from free caustic alkali, sodium carbonate, and organic impurities.

A works' chemist usually determines the proportion of *glycerol* by closely simulating the method of purification and recovery practised in the glycerin department of the works. In commercial analysis, provided sulphur compounds be absent, 1000 grms. are heated to boiling and are acidified with hydrochloric acid, when fatty acids, etc., separate on the top as an oily layer. This is filtered off, the filtrate is made neutral and lead acetate is added. The precipitate is filtered off and the clear solution boiled down. The salt which separates is scooped out with a spoon, and sucked dry by means of a filter-pump. When finally only a few c.c. of solution are left, these are added to the salt, and the latter is exhausted with a mixture consisting of three measures of alcohol (methylated spirit) and one measure of ether. The alcoholic filtrate is evaporated down on the water-bath, and the crude glycerin thus obtained examined by the acetin method.

In a factory where the purification of the soap lye is closely adapted to the works' process, the determination may be shortened (*Lewkowitsch* [1]) by evaporating the ether-alcohol solution on the water-bath and then rapidly heating to 150° C., weighing, burning off the glycerin, and weighing again. The difference corresponds to the contents of pure glycerol. In the author's laboratory, when closely following the manufacturing process, this abbreviated method, based on a series of experiments carefully checked by the acetin method, gives very satisfactory results.

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[1] *Analyst*, 1903, 106.

If but small quantities of soap lye are available, so many grms. are weighed off as will approximately correspond to 1·2 grms. of pure glycerol, and the glycerol is then determined by the bichromate method in the form given to it by *Hehner*.[1]

The following standard solutions are required :—

1. Solution of potassium bichromate containing 74·564[2] grms. of $Cr_2O_7K_2$ per litre. The exact oxidising value of the solution must be checked by titration with a standardised solution of ferrous sulphate, or of pure ferrous ammonium sulphate, or of pure iron wire.
2. Solution of ferrous ammonium sulphate containing about 240 grms. per litre.
3. Bichromate solution, ten times more dilute than solution 1.

The ferrous solution is accurately standardised upon the stronger bichromate solution, 1 c.c. of which should correspond exactly to 0·01 grm. of glycerol.

The soap lye is slightly diluted, and if it contain notable quantities of soap, is acidified with sulphuric acid ; the fatty acids, etc., are filtered off and the filtrate is then purified by means of lead acetate, or by means of copper sulphate and caustic potash, filtered, and made up to 100 c.c.

25 c.c. of this solution are then run into a beaker previously cleaned with bichromate solution and concentrated sulphuric acid, and 40 c.c. of the concentrated potassium bichromate solution are added. As the bichromate solution is necessarily a strong one, the measuring must be done with the greatest care, and attention must be paid to the temperature of the solution. The standard solutions are kept at the normal temperature by immersing them in a large water-bath during the titration.

12·5 c.c. of concentrated sulphuric acid are added, the beaker is covered with a watch-glass and heated in boiling water for two hours.[3] The excess of bichromate is titrated back with an excess of the ferrous ammonium sulphate solution, and the excess of the latter is ultimately measured by titration with the dilute bichromate solution, using potassium ferricyanide as an indicator.

If the lyes are properly purified, the acetin method leads to results practically identical with those obtained by the bichromate method. If, however, the impurities be not completely removed, then here also the bichromate method yields too high results. This is clearly shown by the numbers given in the following table. Those lyes, the specific gravity of which exceeds 1·2, represent partially concentrated lyes ; all other lyes are original spent soap lyes.

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[1] *Journ. Soc. Chem. Ind.*, 1889, 6.

[2] For O = 16 ; K = 39·1 ; Cr = 52·1.

[3] Richardson and Jaffé (*Journ. Soc. Chem. Ind.*, 1899, 331) consider twenty minutes sufficient. They also shorten the process by dispensing with the dilute bichromate solution. Cp. also Bänninger (*Zeits. f. angew. Chem.*, 1907, 1993).

Comparison of the Acetin and Bichromate Methods for determining the Percentage of Glycerol in Soap Lyes (Lewkowitsch)

No.	Specific Gravity.	Free Alkali as Na_2O.	Glycerol. Per cent.	
			1000 c.c. Method.	Bichromate Method (purified with Copper Sulphate).
		Per cent.		
1	1·120	2·39	5·86	6·62 ; 6·80
2	1·114	0·58	7·36	8·48 ; 8·43
3	1·1216	...	5·70	5·89 ; 5·81
4	1·1025	0·927	6·69	7·45 ; 7·33
5	1·0975	0·452	5·90	5·90 ; 6·09
6	1·1050	0·678	5·25	5·34 ; 5·43
7	1·0925	0·809	6·10	5·92 ; 5·88
8	1·1025	1·6	5·64	5·65
9	1·095	0·863	6·95	6·92 ; 6·93
10	1·2025	1·933	9·75	9·68 ; 9·67
11	1·0925	0·51	6·96	6·95 ; 7·07
12	1·09	0·768	6·62	6·78 ; 6·42
13	1·085	0·657	5·70	5·42 ; 5·45
14	1·22	...	11·57	12·5 ; 12·6
15	...	0·49	3·57	4·59
16	...	...	7·55	7·66 ; 7·69

Fanto[1] proposed to determine the glycerin in soap lyes by the iso-propyl-iodide method (Vol. I. Chap. I.). For reasons detailed above, this method cannot be recommended, since soap lyes contain large amounts of not readily removable impurities which reduce hydriodic acid.

On the large scale the spent soap lyes are subjected to a process of purification consisting in the removal of fatty acids, rosin acids, and other organic impurities. According to *J. W. Yates*[2] treatment with sodium aluminate materially reduces the amount of organic impurities in the finished glycerin. In the case of lyes from best materials the purified liquor contains salt, small quantities of sodium carbonate, and practically pure glycerol. This solution may be evaporated in fire-heated vessels or in tube evaporators, such as are used in sugar works, until the " salting point " is reached, without fear of damaging the heating surface by deposition of salt. The " salting point " is marked by the lyes having acquired the specific gravity of 44° Tw. at 15·5° C. If evaporation is carried beyond this stage, salt is deposited, whilst the specific gravity and percentage of glycerol gradually rise. The vessels in which the evaporation beyond the specific gravity of 44° Tw. is carried on must therefore be provided with suitable stirring and scraping arrangements to remove the salt as it separates, all tube evaporators being liable to incrustation with salt and gradual stopping up of the heating tubes.

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[1] *Zeits. f. angew. Chem.*, 1903, 413.

[2] *Journ. Soc. Chem. Ind.*, 1919, 94 T.

An evaporator which has been found suitable in practice for the concentration of lyes up to the finishing point (*i.e.* until they reach the specific gravity of 1·3), and in which incrustation of the heating surface does not take place, has been designed by *Lewkowitsch*.[1] It is shown in Fig. 24. Two types of the internal heating surface are illustrated by Figs. 25 and 26.[2] In these evaporators the soap lyes are evaporated from the dilute state beyond the "salting point," the salt which falls out being removed by the aid of the vessel fixed at the bottom of the evaporating pan. This vessel can be emptied whilst the contents are kept continuously boiling. The salt is then washed to recover the glycerin.[3] In large installations the lyes may be concentrated in double effet or triple effet vacuum apparatus. A double effet designed by the author on the same principle is illustrated by Fig. 27. This shows a combination of the tube evaporator B with an evaporator illustrated

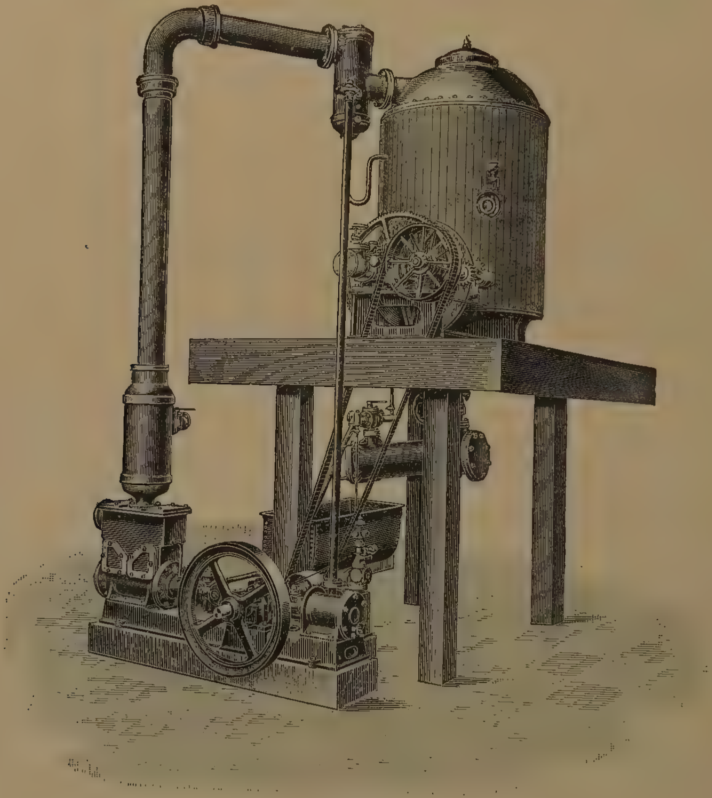

Fig. 24.

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[1] Cp. also Lewkowitsch, "Evaporation in Vacuo of Solutions containing Solids," *Journ. Soc. Chem. Ind.*, 1905, 1149.

[2] Cp. English patents 28,747, 1897; 30,616, 1897.

[3] English patent 14,750, 1909.

by Figs. 24, 25, and 26. The first preliminary concentration up to the "salting point" is carried out in vessel B, whilst the further concentration takes place in vessel A.

The finished glycerin—salt crude glycerin, soap-lye glycerin—has

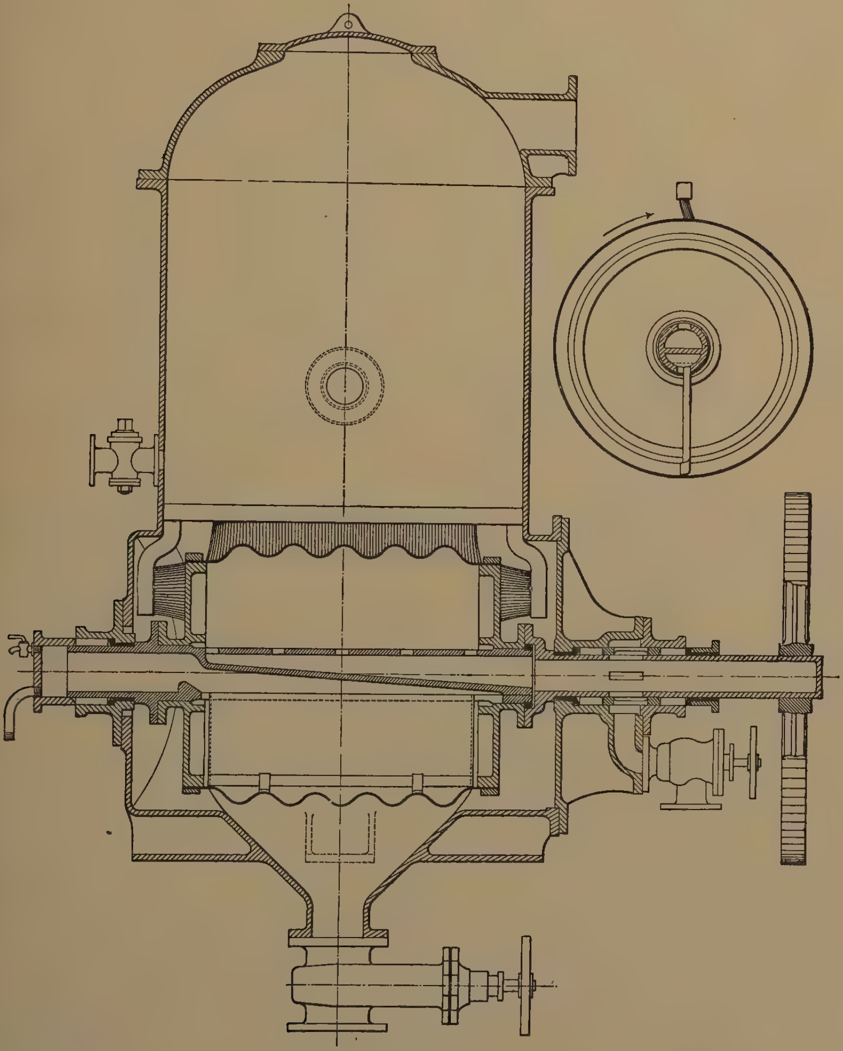

Fig. 25.

a specific gravity of 1·3. It usually contains 80 per cent of pure glycerol and about 10 per cent of salts, the remainder consisting of water and a small amount of organic impurities. It is, however, easy to prepare in the evaporators illustrated here crude glycerin containing as much as 86 per cent of pure glycerol.

The salts in crude soap-lye glycerin should consist preponderantly of common salt and small amounts of sodium carbonate. In low-quality crude glycerins, sodium sulphate, sodium sulphite, sodium sulphide, sodium thiocyanate, and sodium thiosulphate are also found.

The proportion of *organic impurities* in soap-lye glycerin varies considerably, in accordance with the process of purification used, the care of the operator, etc. Some commercial glycerins contain less than 1 per cent of organic impurities (thus representing a glycerin of better quality than "distillation glycerin," "*Twitchell* crude glycerin," and "fermentation glycerin"); others, again, contain large quantities of impurities, consisting of fatty acids, rosin acids, and further of albuminoid substances, gelatin, and hydrocarbons (from bone fat). The organic substances in crude glycerin may give rise to fermentation

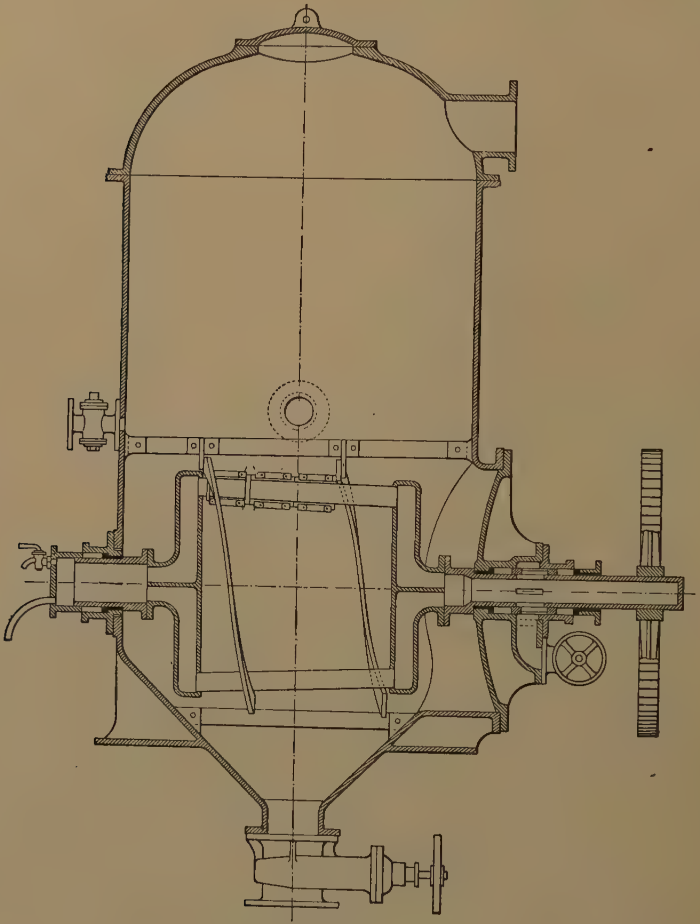

Fig. 26.

on storing, so that, amongst other impurities, trimethyleneglycol will be formed which distils over with the glycerol in the subsequent process of distillation. In other fermented crude glycerins the formation of sulphides has been observed. In the distillate from some impure glycerins the author found organic bases, from which picoline and lutidine could be isolated.[1]

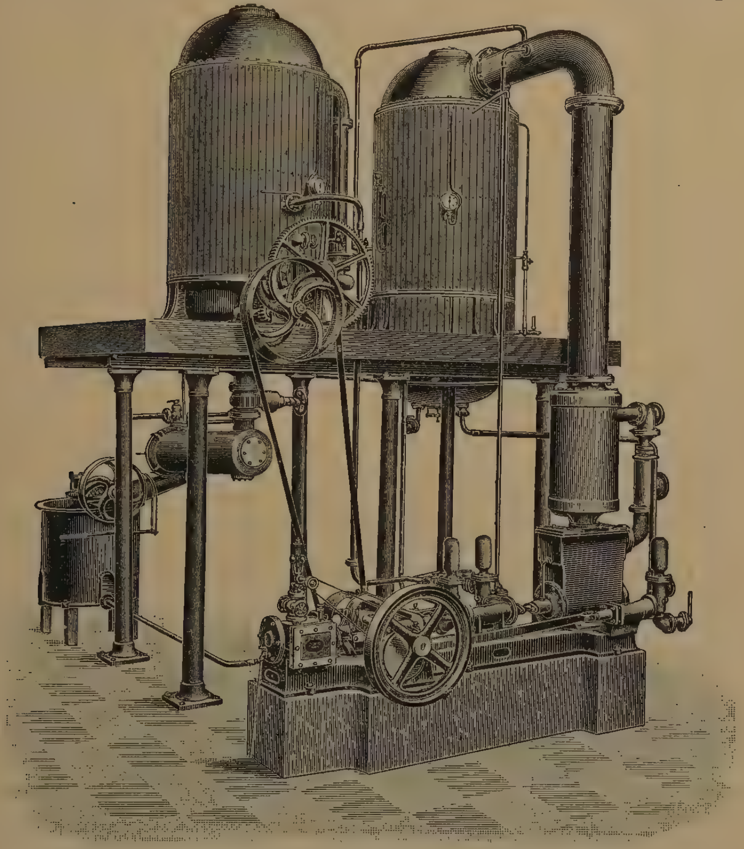

Fig. 27.

The colour of salt crude glycerin is pale yellow to brown, or almost black, according to its state of purity.[2] The taste of good specimens is sweet, qualified, of course, by that of the common salt; impure samples have a most unpleasant garlic-like taste, even if sulphides be absent.

Soap-lye glycerin can be rapidly distinguished from glycerins described under (1), (2), (3), (4) by the large proportion of common salt which it contains (heavy precipitate with silver nitrate), and by its high specific gravity.

---

[1] Cp. also E. Schmitt (*Bull. Soc. Ind. du Norde de la France*, 1905, No. 129), who found in a distilled glycerin organic bases, which were not identified, but were assumed to consist of a mixture of amines (methyl-, ethyl-, etc.), and perhaps also of amides.

[2] Commercial crude glycerins are sometimes bleached by means of formaldehyde-sulphoxylate (Badische Anilin und Soda Fabrik), German patent 224,394; French patent 410,824; English patent 16,260, 1909.

A soap-lye glycerin containing considerable quantities of sulphides, thiosulphates, or sulphites, is almost valueless to the refiner of crude glycerin. A process for the removal of arsenic from glycerin has been proposed by *Davis.*[1]

The determination of *glycerol* is best carried out by the acetin method.[2] The bichromate method in the form prescribed by the International Standard Method [3] is also used in commercial analysis.

The following reagents are required :—

1. *Pure potassium bichromate* powdered and dried at 110-120° C.

2. *Bichromate solution* containing 7·4564 grms. of the reagent 1 in one litre of distilled water. 1 c.c. of the solution = 0·001 grm. of glycerin.

3. *Ferrous Ammonium Sulphate in Crystals.*—This is standardised by dissolving 3·7282 grms. of reagent 1 in 50 c.c. of water. After 50 c.c. of sulphuric acid have been added, a weighed quantity of ferrous ammonium sulphate in a slight excess of the amount required by theory is added. This excess is then titrated back with the dilute bichromate solution.

4. *Silver Carbonate.*—This must be prepared as required for each test by mixing 140 c.c. of an 0·5 per cent solution of silver sulphate with 4·9 c.c. of normal sodium carbonate solution. The precipitated silver carbonate is washed once by decantation and is then ready for use.

5. *Basic Lead Acetate.*—A 10 per cent solution of lead acetate is boiled for one hour with an excess of litharge, the water being replaced as it boils away. The solution is then filtered hot and kept out of contact with carbon dioxide.

6. *Potassium ferri-cyanide solution* containing about 0·1 per cent.

The analysis is carried out as follows :—

20 grms. of the glycerin are weighed off and diluted to 250 c.c. To 25 c.c. of the solution the prescribed amount of silver carbonate is added, and the mixture allowed to stand with occasional shaking for about 10 minutes, after which a slight excess of the basic lead acetate is added, and after allowing to rest for a few minutes the solution is made up to 100 c.c. with an allowance of 0·15 c.c. for the volume of the precipitate. The flask is then well shaken and the solution filtered through a dry filter, the first 10 c.c. being rejected. The addition of the basic lead acetate to a small portion of the filtrate should cause no further precipitation ; otherwise the test must be considered as useless ; 25 c.c. of this filtrate are placed in a beaker which has been cleaned with potassium bichromate and sulphuric acid. Twelve drops of sulphuric acid are added in order to precipitate the excess of lead as

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[1] English patent application 10,051, 1912.

[2] Lewkowitsch, *Chem. Zeit.*, 1889, 93, 191, 659 ; *Journ. Soc. Chem. Ind.*, 1890, 479.

[3] Tortelli and Ceccherelli, *Chem. Zeit.*, 1913, 1505 ; 1914, 3. Cp. also E. Little and B. C. Fenner, *Journ. Amer. Leather Chem. Assoc.*, 1917, 12, 254-257.

sulphate. 3·7282 grms. of the potassium bichromate are added and washed down with 25 c.c. of water; the bichromate is dissolved by imparting a rotary motion to the beaker; 50 c.c. of 50 per cent sulphuric acid are added and the beaker immersed in boiling water for two hours. After cooling, a slight excess of ferrous ammonium sulphate is added and the solution titrated back with the dilute bichromate. The amount of bichromate reduced is calculated to glycerol, 1 grm. of bichromate being equivalent to 0·13411 grm. of glycerol.

Hehner has shown by a number of comparative experiments that the results obtained by the acetin and the bichromate methods agree very well, and the author confirmed this in the second edition of this work.[1] Yet this no longer holds good at present. *Lewkowitsch* [2] proved by a large number of experiments that in the case of many crude glycerins the bichromate method yields appreciably higher results than does the acetin method. This is shown by a number of analyses collated in the following table:—

Comparison of the Acetin and Bichromate Methods for determining the percentage of Glycerol in Soap Crude Glycerin (*Lewkowitsch*)

Description.	Acetin Method.	Bichromate Method (purified with Copper Sulphate).	Bichromate Method (purified with Silver Carbonate and Basic Lead Acetate).
Soap-lye crude .	86·66	86·45	
,, ,,	86·15 ; 86·06	86·01 ; 86·34	
,, ,,	75·02	75·38 ; 75·10	
,, ,,	80·51 ; 80·66	80·37 ; 80·04	
,, ,,	78·93	79·41	
,, ,,	85·94	85·43	
,, ,,	79·84	79·23	
,, ,,	83·05 ; 83·07	83·99 ; 84·65	
,, ,,	78·48 ; 78·55 ; 78·89	81·42 ; 81·60 81·23	
,, ,,	80·46 ; 80·82 ; 80·28 ; 80·61	82·56 ; 83·03 83·23 ; 83·89	
,, ,,	76·56 ; 77·45	79·36 ; 79·01	
,, ,,	81·44 ; 81·19	82·51 ; 82·61	
,, ,,	81·42	82·21	
,, ,,	79·13	81·52 ; 81·94	
,, ,,	75·20	78·79	
,, ,,	72·98	76·04	
,, ,,	72·01	77·44	
Last crude, concentrated further .	74·73	78·35	
Soap-lye crude .	77·31	77·96 ; 78·60	78·30 ; 78·33 ; 78·69
,, ,,	76·53 ; 76·61	78·17 ; 78·24	79·25 ; 79·53

Since the process of bleaching soaps by means of hydrosulphites has come into vogue, the presence of the salts in the glycerin will render the oxidation method still more unreliable.

The acetin method is all the more commendable for the valuation of soap crude glycerin, inasmuch as polyglycerols (residues from the glycerin stills, see p. 395), if admixed with crude glycerin, would be oxidised by the bichromate, and thus calculated to glycerol, whereas the polyglycerols are not converted into esters on boiling with acetic anhydride. *Lewkowitsch*[1] has proved that soap crude glycerins containing polyglycerols show less than 80 per cent in the acetin test. The following table reproduces some analyses :—

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[1] Cp. Lewkowitsch, *Chemical Analysis*, etc., 1898, p. 808.

[2] *Analyst*, 1903, 104.

	Glycerol by Acetin Method. Per cent.
Soap Crude I. containing Still Residues	76·20 ; 76·16 ; 76·45 ; 76·57
„ „ II. „ „ „	77·94 ; 77·68 ; 77·77 ; 77·76
„ „ III. „ more Still Residues	61·40 ; 61·38 ; 61·43 ; 61·09

Ash "Salts."—3–5 grms. of the sample are weighed off accurately in a platinum dish, which is then placed at some distance over a small burner, in order that the glycerol may evaporate off slowly. More heat should only be applied after the glycerol has been driven off, when a bulky carbonaceous residue is obtained. This is heated to a temperature which is just sufficiently high to carbonise the organic matter, but care must be taken that no sodium chloride be volatilised. After cooling, the charred mass is exhausted with water, transferred to a filter, and the filtrate boiled down in the platinum dish on the water bath. The residue, which should be white, is heated (not above 400° C. to avoid loss by volatilisation of sodium chloride), and weighed. Ash contains as a rule sodium carbonate or sodium sulphate, in addition to common salt. If the sodium chloride, carbonate, etc., be required they are estimated by the well-known method of inorganic analysis. The alkali in the ash is determined by titration with standard acid. The carbon on the filter is dried, burnt away, and the weight of the ash (if any) added to the bulk; this is especially necessary if the sample contain lime (cp. *Vizern*).[2]

Free Caustic Alkali.—This is determined by adding to a fairly large quantity of the diluted glycerin barium chloride solution; after filtering off the precipitate the caustic alkali is titrated.

Alkali Carbonates.—10 grms. of the sample are diluted and an excess of standard HCl solution is added. The solution is boiled under a reflux condenser for twenty minutes, the condenser tube washed with carbon dioxide free water, and the excess of acid titrated back with a normal soda solution, using phenolphthalein as indicator. From the amount of Na_2O found here, the Na_2O existing as free caustic is deducted, leaving the Na_2O existing as carbonate.

Organic Impurities.[3]—10 grms. of the sample are weighed off into a 100 c.c. flask, diluted with water and sufficient normal HCl solution added in order to reduce the alkalinity to 0·2 per cent of Na_2O. This amount should not be exceeded, as the presence of a somewhat large excess of soda gives rise to the formation of polyglycerols on heating. In order to prevent the loss of organic acids, if the glycerin be acid an amount of normal sodium carbonate solution must be added sufficient to bring the excess of soda up to 0·2 per cent Na_2O. The solution is made up to 100 c.c., and 10 c.c. are measured off into a weighed platinum dish (2·5″ in diameter and 0·5″ deep). In the case of glycerins containing high amounts of organic residue less solution should be evaporated. The dish is placed on a water bath until most of the water is evaporated, after which it is placed in an oven at about 140° C. until most of the glycerin has been driven off. After cooling, about 1 c.c. of water is added and the residue dissolved. The water is then driven off on the water bath and the dish placed in the oven at 160° C., where it is allowed to remain for one hour. The treatment is repeated until constant weight is attained. A correction must be made for the amount of alkali or acid added. A method for the determination of trimethyleneglycol due to *Cocks and Salway*[1] consists in distilling off 30 per cent of the crude glycerin under reduced pressure and determining the amount of glycerol by the acetin method, and the specific gravity of the distillate. The amount of trimethyleneglycol present is found by referring to curves obtained from mixtures of known composition.

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[1] *Chem. Zeit.*, 1889, 659.

[2] *Journ. Chem. Soc.*, 1890, Abstr., 835.

[3] International Standard Methods, 1911.

From the weight of the total residue the ash is deducted, and the remainder is returned as organic residue at 160° C.

If the amount of organic residue is high it may be treated by the acetin method and the result calculated to glycerol, which is deducted from the total glycerin found by the acetin method.

Fatty acids are detected by acidifying the diluted glycerin with hydrochloric acid.

Arsenic is detected as described, p. 408.

The detection of sulphides, sulphites, and thiosulphates in the crude glycerin is of importance for purposes of valuation. The presence of *sulphides* is ascertained by testing with paper saturated with alkaline lead nitrate solution. To detect traces of sulphides down to $\frac{1}{100000}$th part (*Ferrier*[2]) a few c.c. of the solution are placed in a small flask, and four or five drops of hydrochloric acid are added, as well as a pinch of sodium bicarbonate. The liquid is carefully heated to boiling, and a paper moistened with alkaline lead nitrate held over the flask.

Thiosulphates and *sulphites* are detected by treating the diluted glycerin with a few c.c. of a solution of barium chloride and filtering off the precipitate containing carbonate, sulphate,[3] and *sulphite*. To the clear filtrate two or three drops of hydrochloric acid and a few drops of a potassium permanganate solution are added. If the glycerin contains even less than $\frac{1}{100000}$th part of *thiosulphate*, a distinct turbidity is produced.

The detection of sulphites is effected by washing the precipitate on the filter with boiling water, stirring it up with a little water, and adding to this mixture starch solution and a few drops of iodine solution. In the presence of sulphites the blue coloration disappears with more or less rapidity, whilst in their absence the blue colour is permanent.

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[1] *Journ. Soc. Chem. Ind.*, 1922, 19 T.

[2] *Ibid.*, 1893, 471.

[3] Dobbin, *Pharm. Journ.*, 1900, 182, has shown that small quantities of barium sulphate are soluble in the presence of considerable amounts of thiosulphate.

Another method by which to detect sulphides, sulphites, and thiosulphates in presence of sulphates (which may occur in soap lyes to a notable extent) has been proposed by *Browning and Howe.*[1] The solution should be made *slightly* alkaline; zinc acetate is then added in distinct excess. The precipitate of zinc sulphide is filtered off and tested by treating with mineral acid. The filtrate is acidified with acetic acid, and the sulphates precipitated by barium chloride. Iodine solution is added to the filtrate until a permanent coloration is obtained; the excess of iodine is removed by stannous chloride and a few drops of hydrochloric acid (to prevent formation of basic stannic salts). If a precipitate be obtained at this stage the presence of sulphites is proved. The precipitate is filtered off, and the filtrate treated with bromine water. The solution is then again decolorised with stannous chloride; a precipitate would indicate the presence of thiosulphates.

For the quantitative estimation of sulphides, sulphites, thiosulphates, and sulphates in presence of each other the reader must be referred to the original papers quoted in the footnote.[2]

Midway between "crude glycerins" and "distilled glycerins" stand the "commercial refined" glycerins obtained from saponification of crude glycerin by treatment with char or other bleaching agents.[3] Such refined glycerin is almost white, and is used for various purposes in the arts as a substitute for distilled glycerin.

Distillation crude glycerin cannot be obtained white in this manner; the same holds good of the other crude glycerins described above.

SYNTHETIC GLYCERIN

The production of glycerin by the chlorination of propylene[4] or by the oxidation of allyl alcohol by means of potassium chlorate in the presence of osmium[5] is not likely at any rate in the immediate future to become practical on a commercial scale. More hopeful, however, is the conversion of the sugars contained in crude molasses into glycerin.

It has been known for many years that the alcoholic fermentation of wine gave rise to the formation of small amounts of glycerin, and investigations were carried on in a desultory fashion to discover means of increasing the yield. The stimulation produced by the recent shortage of glycerin resulted in the manufacture of glycerin by this process becoming possible under the economic conditions produced by the war. Whether the glycerin so produced can compete in normal times with that produced by the hydrolysis of oils and fats is somewhat doubtful. There is a considerable amount of alcohol produced concurrently with the formation of glycerol, sufficient in quantity, it is stated, to cover the cost of the raw material.

In the United States a method was worked out by *J. Eoff, W. V.*

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[1] *Zeits. f. anorg. Chem.*, 1898, 371.

[2] Lunge and Smith, *Journ. Soc. Chem. Ind.*, 1883, 463; Richardson and Aykroyd, *ibid.*, 1896, 171; Lunge and Segaller, *ibid.*, 1900, 221.

[3] Badische Anilin und Soda Fabrik, English patent 16,260, 1909; German patent 224,394; French patent 410,824; United States patent 1,089,775.

[4] A. Heinemann, English patent 12,366, 1913; French patent 458,398, 1913.

[5] K. A. Hofmann, O. Ehrhart, and O. Schneider (*Berichte*, 1913, 165).

Linder, and *G. F. Beyer*[1] which consisted in fermenting crude black molasses with a yeast (a variety of *S. Ellipsoideus*) in the presence of a small amount of sodium carbonate and ammonium chloride, the temperature being kept at 30° C. for five days. The dilute solution so obtained contained 3·1 per cent of glycerol and 6·75 per cent of alcohol, the yield of glycerol being about 25 per cent of the weight of sugar taken. Of this amount no more than half could be recovered. The fermented solution, after purification by means of ferrous sulphate followed by milk of lime, was concentrated in a vacuum evaporator and distilled. The distilled glycerin had the specific gravity 1·2616, and contained organic residue 0·058 per cent and ash 0·009 per cent. In Germany the method was developed by *Connstein and Ludecke*,[2] who obtained a yield of from 20 to 25 per cent on a manufacturing scale by fermenting sugar in the presence of sodium sulphite, the production being, it is stated, 1000 tons a month. The glycerin in both cases behaved normally during nitration.

The determination of the glycerol in the crude fermented liquor offers some difficulties, inasmuch as any unchanged sugar would be oxidised by the potassium bichromate and appear in the result as glycerol. The isopropyl iodide method (Vol. I. p. 459) is stated to give good results. For the details of a method of distilling off the glycerol quantitatively the original papers by *K. Fleischer*[3] must be consulted.

2. DISTILLED GLYCERIN—DYNAMITE GLYCERIN

These glycerins are obtained from the different crude glycerins described above, by distillation. The distillation is carried out either under ordinary pressure or in a vacuum. In either case the distillation is supported or accelerated by the aid of superheated steam The latter method is the one mostly in vogue at present. Some manufacturers work off in one batch a certain amount of crude glycerin (depending on the size of the stills), others resort to continuous distillation, the still being fed as the glycerin distils off. The successful distillation of crude glycerin does not depend so much on the kind of apparatus used as on the skill and care of the operator. A large number of special apparatus and stills have been patented,[4] but owing to the fact just pointed out (viz. that success depends more on the skill of the operator than on the particular apparatus employed), the details of the methods are considered valuable secrets. For it rests solely with the mode of working—especially in the case of soap-lye glycerin—as to whether one distillation suffices to obtain a satisfactory product, or whether the once distilled glycerin must be distilled again. If the distillation be not conducted carefully, the once distilled glycerin is so strongly contaminated with sodium chloride and organic impurities (especially volatile acids and even polyglycerols) that a second distillation becomes imperative.

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[1] *Journ. Ind. and Eng. Chem.*, 1919, 842; United States patent 1,288,398, 1918 (presented to the public).

[2] *Berichte*, 1919, 52, 1385-1391. Cp. also K. Schweitzer, *Chem. Zeit.*, 18-19, 1919; and A. Koch, German patent 338,734, 1917.

[3] *Zeitsch. Anal. Chem.*, 1921, 60, 330-338.

[4] Cp. United States patent 881,525 (F. J. Wood) and 910,440 (see *Chem. Zeit. Rep.*, 1909, 147); Marx and Rawolle, German patent 217,689; United States patent 910,440.

The yield obtainable from crude glycerin depends likewise on the care of the operator. The losses incurred by unsatisfactory distillation are large, and range, in cases within the experience of the author, from as much as 15 to even 40 per cent. A large proportion of the loss is due to destruction of glycerol with the formation of volatile acids and acrolein on the one hand, and to the formation of polyglycerols on the other hand. The polyglycerols are mainly found in the *still residues* (*glycerin foots*).

Distilled glycerin is used for many purposes in the arts, such as for filling gas-meters and hydraulic jacks, in the manufacture of copying inks,[1] carbon papers, waterproof paper, toilet soaps, " sizes " for textiles, and for the production of plastic masses (printing rollers, hectograph mass),[2] and for impregnating tissues.[3] The bulk of distilled glycerin is, however, employed in the manufacture of high explosives, such as dynamite, blasting gelatine, cordite, etc.

These glycerins, being prepared by distillation, contain a very small amount of ash, and are thereby easily distinguished form crude glycerins. Distilled glycerins are further differentiated from crude glycerins by not giving a precipitate with lead acetate.

The commercial distilled glycerins vary in colour from yellow to white; they also vary in their content of glycerol, according to their specific gravities, which range between 1·220 and 1·260.

The percentage of *glycerol* may be ascertained with approximate accuracy by referring to the tables of specific gravities given on p. 398. The small amount of ash these glycerins contain has, however, some influence on the specific gravity. If great accuracy be required, the glycerol should be determined by the acetin method or the bichromate method, although it must be again repeated that the bichromate method has a tendency to yield too high results.

Dynamite glycerin represents that quality of distilled glycerin which has a specific gravity of 1·261 to 1·263. According to the care with which it has been manufactured, its colour varies from a deep yellow to a pale colour.

Owing to the risks to which a manufacturer of dynamite is exposed if the glycerin be impure, the conditions to which a dynamite glycerin should conform are usually laid down in contracts between buyer and seller. Thus the following conditions are stipulated :—

Specific Gravity.—This should not be less than 1·261 at 15·5° C. (For the method of determination, see p. 400.) The specific gravity test is a very important one, as an apparently high percentage of glycerol may be found by the bichromate method, or even in the acetin test, due to the presence of trimethyleneglycol, which occurs in commercial glycerin obtained from low-class greases (*Noyes and Watkin*;[1] cp. above, p. 378). The presence of trimethyleneglycol may be suspected if a low specific gravity is found concurrently with an apparently high percentage of glycerol. *Barton*[2] proposes to heat the glycerin to 225°-230° C. for two hours and then to take again the specific gravity; the second value is termed "permanent specific gravity." Any hydrocarbons present in glycerins from bone fat are thus volatilised. The "permanent specific gravity" will always be higher than the specific gravity of the sample, as the last traces of water are volatilised: trimethyleneglycol (boiling point 214°-217° C.) also will most likely be driven off by heating.

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[1] Beyer, German patent 224,637, 229,467; Hochstetter patents an ink prepared from a mixture of glycerin and a sulphonated oil. Unites States patents 928,450, 928,915.

[2] Cp. German patent 202,849 (W. H. Brownlow); Betzer, German patent 231,460.

[3] Wechsler, French patent 425,777.

Lime, magnesia, and *alumina* should be absent.

Chlorine.—Traces only are permissible; the glycerin must not become milky with silver nitrate. Milkiness is observed when the proportion of sodium chloride lies between 0·025 and 0·01 per cent (as the author has ascertained by a number of experiments). The quantitative determination of sodium chloride is, however, unnecessary.

Arsenic.—Only minute traces are tolerated. The test is made by making the glycerin *just* alikaline with a minute quantity of ammonia, and adding silver nitrate. No yellow precipitate should appear. As this precipitate is soluble in ammonia, an excess of the latter must be avoided. Greater certainty is obtained by *Gutzeit's* reaction (see p. 408), using mercuric chloride.

Organic Impurities.—The glycerin must not become brown or black within ten minutes after the addition of a few drops of silver nitrate to the diluted glycerin.

Total Residue.—This is determined as described, p. 388. It should not exceed 0·25 per cent of the dynamite glycerin. If there be reason to suspect the presence of organic bases in the sample, a small amount of hydrochloric or nitric acid is added, when the hydrochloride or nitrate of the bases will be obtained in the residue.

Free Acids.—The glycerin should not be acid to litmus, nor should it contain fatty acids; the test for volatile fatty acids (which occur at present more frequently in some dynamite glycerins than used to be the case some years ago) is carried out as described under chemically pure glycerin, p. 406. Some specifications stipulate that on passing nitrous acid fumes through the glycerin it must not curdle, it being supposed that oleic acid would thus be detected.[3] It will be found more suitable to add hydrochloric acid to one volume of glycerin diluted with two volumes of water; a turbidity would indicate the presence of insoluble fatty acids.

Nitration and Separation Test.—A sample of glycerin may prove satisfactory in all preceding tests, and yet be totally unfit for the manufacture of nitroglycerin. The suitability of a sample of dynamite glycerin must therefore be determined by the following process, which simulates large scale operations.[4]

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[1] *Journ. Soc. Chem. Ind.*, 1896, 207.

[2] *Ibid.*, 1895. 516.

[3] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1908, 199.

[4] Lewkowitsch, *Chem. Zeit.*, 1895, 1423; *Journ. Soc. Chem. Ind.*, 1895, 1073.

375 grms. of a mixture, consisting of one part (by weight) of nitric acid, specific gravity 1·5, and two parts (by weight) of sulphuric acid, specific gravity 1·845, previously cooled down to the ordinary temperature in a closed vessel, are weighed off in a beaker of about 500 c.c. capacity. A thermometer, which serves during nitration as a stirrer, is then introduced into the acid, and the beaker is immersed in a capacious vessel filled with cold water, or, if necessary, with ice. A stream of cold water is kept running through the vessel by means of a stout india-rubber tubing, $\frac{3}{4}''$ diameter, coiled at the bottom of the vessel. It is very important that the india-rubber tubing should be securely fastened to the water-tap, if the latter be near the operator, as it may easily happen that if the tube is thrown off the tap by the pressure of the water in the pipe, water is splashed into the acid, whereby the temperature may rise suddenly, so that an explosion ensues. The author uses[1] thin-walled beakers, so that they can be rapidly broken in case the temperature rises to a point of danger; the rapid discharge of the mixed acids and nitroglycerin into the large mass of water effectively prevents an explosion.

When the temperature of the acids has fallen to about 12° to 15° C., 50 grms. of the sample of glycerin, weighed off in a beaker having a spout, are allowed to fall into the acids, drop by drop. The liquid is constantly stirred with the thermometer, and the temperature is observed after the addition of every single drop of glycerin. Considering the danger attending this operation, the inexperienced analyst should be instructed in the carrying out of the test by a practised operator. If this be not feasible, the safest plan is to proceed in the manner described, *i.e.*, add cautiously drop by drop, stirring all the while, so that no overheating may take place *locally*, and never allow the temperature to exceed 30° C. No addition of a further drop of glycerin must be made until the temperature has fallen below 25° C. (An experienced operator will, of course, proceed a little more rapidly.)

When all the glycerin has been introduced in this manner, the mixture is stirred for a short period, until the temperature has fallen to about 15° C., when it is transferred to a separating funnel, which must be absolutely dry. The safest plan is to rinse the funnel with concentrated sulphuric acid.

If the dynamite glycerin is of good quality, the nitroglycerin formed will rapidly rise and separate in a few minutes as an oily, somewhat turbid layer on the top of the spent acids. The quicker the separation into two well-defined layers takes place the better is the glycerin. If flocculent matter be noticeable in the nitroglycerin layer, or if the separation be slow, and an intermediate layer of this flocculent substance render the line of separation indistinct, the sample is unsuitable for dynamite making. In some cases, owing to the nitroglycerin being honeycombed with this flocculent substance, several hours are required for separation. Such a glycerin must, of course, be rejected.

Owing to the somewhat dangerous nature of this test in an analyst's laboratory, the quantity of glycerin employed has been gradually reduced from 50 to 15 grms. This should, however, be the lowest permissible quantity, as the indications furnished by the nitration test become unreliable if only 10 grms. of glycerin be used.[1]

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[1] Lewkowitsch, *Chem. Zeit.*, 1895, 1423; *Journ. Soc. Chem. Ind.*, 1895, 1073.

The *quantitative* determination of the yield of nitroglycerin is conveniently combined with the nitration test. In that case the accurate quantity of glycerin employed is either determined by weighing back the empty beaker, or the beaker is rinsed out with the mixture of acids and nitroglycerin. The former method is the safer one. After separation of the nitroglycerin, the acid layer is carefully drawn off, and the nitroglycerin slightly agitated without shaking, so that any drops of acid adhering to the vessel are made to collect. This acid is carefully drawn off, and the nitroglycerin washed once with water at 35°-40° C., then once or twice with a 20 per cent solution of sodium carbonate, and then again with water. The nitroglycerin is next transferred to a suitable burette, in which the adhering water is made to rise to the top. The volume is read off, and the number of c.c. multiplied by 1·6, which is the specific gravity of pure nitroglycerin (the specific gravity of the product may be determined if desired); another method is to weigh the nitroglycerin after separating the water and filtering over salt to remove moisture.

It is evident that this process yields only approximate results, especially so as nitroglycerin is slightly soluble in water. The method is, however, satisfactory for the commercial valuation of dynamite glycerin. The yield of nitroglycerin should be over 210 per cent. The quantity of nitroglycerin contained in the washings (recovered on the large scale by the so-called after-separation) is disregarded. The theoretical yield of nitroglycerin from glycerol is 246·7 per cent.

It is, of course, necessary to destroy the nitroglycerin. This is done best by spreading out a sufficient quantity of dry sawdust in a moderately thick layer in an open space (not too near a building), and allowing the nitroglycerin to drop from a separating funnel on to it whilst the operator carries the funnel along the sawdust, so as to distribute the nitroglycerin in a slender continuous trail, taking care that no pool is formed. By applying a lighted match to one end of the trail the nitroglycerin will burn away quickly. The waste acids should be destroyed in a similar manner; when these are brought into contact with sawdust a violent reaction sets in, but no explosion need be feared if the nitroglycerin has been separated off carefully.

Still Residues ("Glycerin Foots")[2]

(1) The still residues from the distillation of *crude glycerins* low in ash (see crude glycerins (1), (2), (3), (4), p. 374) consist chiefly of polyglycerols and of notable amounts of salts, as the mineral matters originally contained in the crude material naturally accumulate in the residues.

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[1] Cp. F. Nathan, *Journ. Soc. Chem. Ind.*, 1908, 193.

[2] E. Lewis, *Journ. Soc. Chem. Ind.*, 1922, 97 T.

They are used in the manufacture of shoe-blacking. Recently *Claeszen*[1] proposed their technical employment (in place of glycerin) in the production of plastic masses (printing rollers, hectograph mass), sizes for textiles, and for waterproofing paper.

(2) The still residues from *soap lye crude* contain much larger amounts of salts than those described under (1). The residues obtained in the *course of distillation* retain such considerable amounts of glycerol, in addition to polyglycerols, salt, sodium carbonate, sodium acetate, and sodium salts of other organic non-volatile acids, that the accumulated residues are worked up for the recovery of glycerin. The residues are therefore boiled up with water, and dilute hydrochloric (or sulphuric) acid is added to decompose carbonate of sodium and the organic sodium salts. The organic non-volatile acids collect on the surface of the liquid as a resinous mass, which is removed. The liquor is then filtered and concentrated separately, or is admixed to the ordinary soap lyes. It should be noted that during the concentration of these liquors acetic acid volatilises; it is therefore advisable to concentrate the lyes separately and distil the recovered glycerin. A patented method[2] for the removal of the glycerin consists in converting it into its oleic acid ester.

The finally obtained still residues are too low in content of glycerin to be reworked, and are therefore employed for making shoe-blacking, etc.

The proportion of glycerol is best determined by the acetin method.

Polymers of glycerin are prepared on a commercial scale by heating the glycerin with small amounts of caustic soda or sodium acetate,[3] or by heating the glycerin to 240° C. in a current of carbon dioxide.[4] Thus, by using 0·5 per cent of sodium carbonate as an accelerator, the patentees claim that the final product contains 40 per cent of diglycerol. The presence of nitrated diglycerol in nitroglycerin lowers the freezing point.

3. CHEMICALLY PURE GLYCERIN

The glycerins described under 2 still contain a small amount of impurities, so that they cannot be employed for pharmaceutical and dietetic purposes. The once distilled glycerin must therefore be subjected to a second distillation. If the distillation is carried out with sufficient care, the distillates yield, after concentration and treatment with char, the chemically pure glycerin of commerce.

At a time when the art of preparing chemically pure glycerin was not so far advanced as it is to-day, some chemically pure glycerin was manufactured by allowing glycerin to crystallise, and by removing the impurities in a centrifugal machine. This process has, however, been abandoned, not only on account of its costliness, but also on account of the inferiority of the product as compared with the best brands of chemically pure glycerin obtained by careful distillation, for it was found that the crystals were apt to occlude impurities.

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[1] German patent 198,711; French patents, 392,884, 393,341.

[2] German patent 302,826.

[3] Fleming, United States patent 13,234, 978,443, 969,159; English patent 15,829, 1910; Canadian patent 136,991.

[4] Nobel, Rintoul and Innes, English patent 24,608, 1910.

Chemically pure glycerin is obtainable in commerce in different (strengths) concentrations. The commercial preparations are:—Chemically pure glycerin of 1·24 specific gravity, chemically pure glycerin of 1·25 specific gravity, and chemically pure glycerin of 1·26 specific gravity.

The chemically pure glycerin of the highest specific gravity should approach as nearly as possible the chemical substance glycerol, the properties of which have been described, Vol. I. Chap. III.

Such glycerin is odourless, colourless, has a pure sweet taste, and is as free from impurities as it is possible to prepare a substance on a large scale. The preparation demanded by the Pharmacopœia is the purest commercial article; it should consist of glycerol and small amounts of water.

Provided the chemically pure glycerin satisfies the qualitative tests described below, the proportion of glycerol can be ascertained by merely determining the **specific gravity** of the sample. J. Kellner[1] recommends the determination of the viscosity.

The following tables give the specific gravities of aqueous solutions of chemically pure glycerin, as determined by *Lenz*,[2] *Strohmer*,[3] *Gerlach*,[4] and *Nicol*.[5] Cp. also Vol. I. p. 249.

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[1] *Chem. Zentr.*, 1921, 92, ii. 834.

[2] *Zeits. f. analyt. Chem.* 19, 302.

[3] *Monatsh. f. Chem.*, 1884 (5), 61.

[4] *Chemische Industrie*, 7, 281.

[5] *Pharm. Journ. and Transact.*, 1887, 297.

TABLE

Specific Gravities of Aqueous Solutions of Chemically Pure Glycerin

Glycerol. Per cent.	Lenz.	Strohmer.	Gerlach.		Nicol.
	Spec. Grav. at 12°-14° C. Water at 12° C.=1.	Spec. Grav. at 17·5° C. Water at 17·5° C.=1.	Spec. Grav. at 15° C. Water at 15° C.=1.	Spec. Grav. at 20° C. Water at 20° C.=1.	Spec. Grav. at 20° C. Water at 20° C.=1.
100	1·2691	1·262	1·2653	1·2620	1·26348
99	1·2664	1·259	1·2628	1·2594	1·26091
98	1·2637	1·257	1·2602	1·2568	1·25832
97	1·2610	1·254	1·2577	1·2542	1·25572
96	1·2584	1·252	1·2552	1·2516	1·25312
95	1·2557	1·249	1·2526	1·2490	1·25052
94	1·2531	1·246	1·2501	1·2464	1·24790
93	1·2504	1·244	1·2476	1·2438	1·24526
92	1·2478	1·241	1·2451	1·2412	1·24259
91	1·2451	1·239	1·2425	1·2386	1·23990
90	1·2425	1·236	1·2400	1·2360	1·23720
89	1·2398	1·233	1·2373	1·2333	1·23449
88	1·2372	1·231	1·2346	1·2306	1·23178
87	1·2345	1·228	1·2319	1·2279	1·22907
86	1·2318	1·226	1·2292	1·2252	1·22636
85	1·2292	1·223	1·2265	1·2225	1·22365
84	1·2265	1·220	1·2238	1·2198	1·22094
83	1·2238	1·218	1·2211	1·2171	1·21823
82	1·2212	1·215	1·2184	1·2144	1·21552
81	1·2185	1·213	1·2157	1·2117	1·21281
80	1·2159	1·210	1·2130	1·2090	1·21010
79	1·2122	1·207	1·2102	1·2063	1·20739
78	1·2106	1·204	1·2074	1·2036	1·20468
77	1·2079	1·202	1·2046	1·2009	1·20197
76	1·2042	1·199	1·2018	1·1982	1·19925
75	1·2016	1·196	1·1990	1·1955	1·19653
74	1·1999	1·193	1·1962	1·1928	1·19381
73	1·1973	1·190	1·1934	1·1901	1·19109
72	1·1945	1·188	1·1906	1·1874	1·18837
71	1·1918	1·185	1·1878	1·1847	1·18565
70	1·1889	1·182	1·1850	1·1820	1·18293
69	1·1858	1·179	...	...	1·18020
68	1·1826	1·176	...	...	1·17747
67	1·1795	1·173	...	...	1·17474
66	1·1764	1·170	...	...	1·17201
65	1·1733	1·167	1·1711	1·1685	1·16928
64	1·1702	1·163	...	...	1·16654
63	1·1671	1·160	...	...	1·16380
62	1·1640	1·157	...	...	1·16107
61	1·1610	1·154	...	...	1·15834
60	1·1582	1·151	1·1570	1·1550	1·15561
59	1·1556	1·149	...	...	1·15288
58	1·1530	1·146	...	...	1·15015
57	1·1505	1·144	...	...	1·14742
56	1·1480	1·142	...	...	1·14469
55	1·1455	1·140	1·1430	1·1415	1·14196
54	1·1430	1·137	...	...	1·13923
53	1·1403	1·135	...	...	1·13650
52	1·1375	1·133	...	...	1·13377
51	1·1348	1·130	...	...	1·13104
50	1·1320	1·128	1·1290	1·1280	1·12831
45	1·1183	...	1·1155	1·1145	1·11469
40	1·1045	...	1·1020	1·1010	1·10118
35	1·0907	...	1·0885	1·0875	1·08786
30	1·0771	...	1·0750	1·0740	1·07469
25	1·0635	...	1·0620	1·0610	1·06166
20	1·0498	...	1·0490	1·0480	1·04884
15	1·0374	...	...	...	1·03622
10	1·0245	...	1·0245	1·0235	1·02391
5	1·0123	...	...	...	1·01184
0	1·0000	...	1·0000	1·0000	1·00000

The purity of the specimen of chemically pure glycerin used by *Lenz* for his determinations was ascertained by ultimate analysis. *Strohmer* employed crystallised glycerin freed from water by repeated pressing between folds of filter paper. *Gerlach* prepared his most concentrated glycerin by boiling down a chemically pure glycerin of specific gravity 1·220, until it reached a temperature of 290° C., when the boiling point remained constant. *L. W. Bosart*,[1] however, points out that *Gerlach's* table for specific gravities at 20° C. is inaccurate.

The specific gravities of aqueous solutions for each degree below 50 per cent are given in the tables, pp. 402 and 403.

Specific gravities found at temperatures other than those given in the table may be corrected with the aid of the numbers contained in the following table (*Gerlach*) :—

Expansion of Aqueous Solutions of Glycerin. Volume at 0° C. – 10,000

Glycerol	Volume at 0° C.	Volume at 10° C.	Volume at 20° C.	Volume at 30° C.
Per cent.				
0	10,000	10,001·3	10,016·0	10,041·5
10	10,000	10,010	10,030	10,059
20	10,000	10,020	10,045	10,078
30	10,000	10,025	10,058	10,097
40	10,000	10,030	10,067	10,111
50	10,000	10,034	10,076	10,124
60	10,000	10,038	10,084	10,133
70	10,000	10,042	10,091	10,143
80	10,000	10,043	10,092	10,144
90	10,000	10,045	10,095	10,148
100	10,000	10,045	10,096	10,150

The numbers for other temperatures are found by interpolation. The co-efficient expansion as determined by *Comey and Backus*[2] was, at 20° C., 0·000610; at 25° and at 30° C., 0·000615 and 0·000620 respectively. For temperatures between 15° and 20° C. the specific gravity can be calculated from the numbers given by *Gerlach* (table, p. 398) by means of the following formula :—

$$s_t = s_1 + \frac{t-15}{5}(s_2 - s_1),$$

where

s_1 is the specific gravity of the glycerin at 15° C. , Water at 15° C. = 1.
s_2 ,, ,, ,, ,, 20° C. ,, 20° C. = 1.
s_t ,, ,, ,, ,, t° C ,, t° C. = 1.

A few of the numbers contained in the tables, pp. 398 and 403, have been controlled by ultimate analysis by *Morawski*.[3] His results show that *Lenz's* figures are, as a rule, a little too low, and *Strohmer's* a little too high, whereas *Gerlach's* and *Skalweit's* values agree both amongst themselves and with the results of elementary analysis.

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[1] *Journ. Ind. Eng. Chem.*, 1921, 13, 944-945.

[2] *Ibid*, 1910, 11.

[3] *Chem. Zeit.* 13, 431. It may be added here that *Morawski's* method of determining the percentage of glycerol by means of lead oxide has been shown by *Lewkowitsch* to yield unreliable results. (*Chem. Zeit.*, 1889, 94. Cp. also *Chem. Anal. of Oils, Fats, and Waxes*, 2nd edition, 1898, p. 801.)

The specific gravity of the sample is determined by the methods described, Vol. I. Chap. V. In the case of the most concentrated glycerin a slight complication arises if air bubbles become entangled in the liquid, as they rise only very slowly to the top of the viscous liquid at the ordinary temperature. If the hydrostatic balance be used, as is stipulated in many contracts (especially for dynamite glycerin, p. 391), the determination may require hours. Air bubbles are avoided by pouring the glycerin, carefully held in a slightly inclined position, along the side of the cylinder (of the hydrostatic balance).

Hehner[1] recommends to fill a *Sprengel* tube with the glycerin at a higher temperature than the ordinary one with the aid of the filter-pump, and then to immerse the tube in water of the normal temperature; for any other temperature a correction of 0·00058 for each degree centigrade must be made. By means of this factor *Richmond* calculated the numbers given by *Lenz* to 15·5° C.:—

Glycerol.	Specific Gravity at 15·5° C.	Glycerol.	Specific Gravity at 15·5° C.
Per cent.		Per cent.	
100	1·2674	87	1·2327
99	1·2647	86	1·2301
98	1·2620	85	1·2274
97	1·2594	84	1·2248
96	1·2567	83	1·2222
95	1·2540	82	1·2196
94	1·2513	81	1·2169
93	1·2486	80	1·2143
92	1·2460	79	1·2117
91	1·2433	78	1·2090
90	1·2406	77	1·2064
89	1·2380	76	1·2037
88	1·2353	75	1·2011

The author prefers the following method:—The sample is warmed in a closed bottle by immersing in warm water until the liquid has become perfectly free from air bubbles. The glycerin is allowed to cool in the closed bottle, preferably to the normal temperature, and then carefully transferred to an ordinary specific gravity bottle provided with a perforated stopper. After this has been pushed home, the minute drop of glycerin squeezed out is wiped off with a linen cloth and the bottle is taken out of the water-bath. A number of comparative experiments, in which those made with the *Sprengel* tube were considered the standard, proved that the specific gravities are correct to the fourth decimal if the weights are reduced to vacuum. Complicated calculation is avoided by determining once for all the necessary corrections for the picnometer. Suppose p be the weight in air, then the correct weight, P, will be

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[1] *Journ. Soc. Chem. Ind.*, 1889, 8.

$$P = p + p\,R.$$

If brass weights are used, the correctness, R, for the usual range of specific gravities is found from the following table[1] :—

Correction for Weights in Vacuo

Specific Gravity.	R.
1·00	0·00106
1·02	0·00103
1·04	0·00101
1·06	0·00099
1·08	0·00097
1·10	0·00095
1·15	0·00090
1·20	0·00086
1·25	0·00082
1·30	0·00078

Refractive Index.—The percentage of glycerol in a sample can be ascertained rapidly and with accuracy by means of the refractometer.

The numbers given in the following tables, due to *Lens*, *Strohmer*, and *Skalweit*,[2] were determined with *Abbe's* refractometer. According to *Lenz*, the several observations agree amongst each other to a few units of the fourth decimal, whilst the difference in the refractive indices corresponding to 1 per cent of glycerin amounts to 13·5 units of the fourth decimal. By reference to the tables, the percentage of glycerol in a sample can therefore be determined accurately to about 0·5 per cent. For dilute aqueous solutions of glycerol an "immersion refractometer" (see Vol. I. Chap. V.) may be used.

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[1] Landolt, *Optisches Drehungsvermögen*, 1st ed., p. 131.

[2] *Repert. Anal. Chem.* 5, 18.

[Table

Specific Gravities and Refractive Indices of Aqueous Solutions of Chemically Pure Glycerin (*Lenz*)

Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12·5°-12·8° C.	Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12·5°-12·8° C.	Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12·5°-12·8° C.
Per cent.			Per cent.			Per cent.		
100	1·2691	1·4758	66	1·1764	1·4249	32	1·0825	1·3745
99	1·2664	1·4744	65	1·1733	1·4231	31	1·0798	1·3732
98	1·2637	1·4729	64	1·1702	1·4213	30	1·0771	1·3719
97	1·2610	1·4715	63	1·1671	1·4195	29	1·0744	1·3706
96	1·2584	1·4700	62	1·1640	1·4176	28	1·0716	1·3692
95	1·2557	1·4686	61	1·1610	1·4158	27	1·0689	1·3679
94	1·2531	1·4671	60	1·1582	1·4140	26	1·0663	1·3666
93	1·2504	1·4657	59	1·1556	1·4126	25	1·0635	1·3652
92	1·2478	1·4642	58	1·1530	1·4114	24	1·0608	1·3639
91	1·2451	1·4628	57	1·1505	1·4102	23	1·0580	1·3626
90	1·2425	1·4613	56	1·1480	1·4091	22	1·0553	1·3612
89	1·2398	1·4598	55	1·1455	1·4079	21	1·0525	1·3599
88	1·2372	1·4584	54	1·1430	1·4065	20	1·0498	1·3585
87	1·2345	1·4569	53	1·1403	1·4051	19	1·0471	1·3572
86	1·2318	1·4555	52	1·1375	1·4036	18	1·0446	1·3559
85	1·2292	1·4540	51	1·1348	1·4022	17	1·0422	1·3546
84	1·2265	1·4525	50	1·1320	1·4007	16	1·0398	1·3533
83	1·2238	1·4511	49	1·1293	1·3993	15	1·0374	1·3520
82	1·2212	1·4496	48	1·1265	1·3979	14	1·0349	1·3507
81	1·2185	1·4482	47	1·1238	1·3964	13	1·0332	1·3494
80	1·2159	1·4467	46	1·1210	1·3950	12	1·0297	1·3480
79	1·2122	1·4453	45	1·1183	1·3935	11	1·0271	1·3467
78	1·2106	1·4438	44	1·1155	1·3921	10	1·0245	1·3454
77	1·2079	1·4424	43	1·1127	1·3906	9	1·0221	1·3442
76	1·2042	1·4409	42	1·1100	1·3890	8	1·0196	1·3430
75	1·2016	1·4395	41	1·1072	1·3875	7	1·0172	1·3417
74	1·1999	1·4380	40	1·1045	1·3860	6	1·0147	1·3405
73	1·1973	1·4366	39	1·1017	1·3844	5	1·0123	1·3392
72	1·1945	1·4352	38	1·0989	1·3829	4	1·0098	1·3380
71	1·1918	1·4337	37	1·0962	1·3813	3	1·0074	1·3367
70	1·1889	1·4321	36	1·0934	1·3798	2	1·0049	1·3355
69	1·1858	1·4304	35	1·0907	1·3785	1	1·0025	1·3342
68	1·1826	1·4286	34	1·0880	1·3772			
67	1·1795	1·4267	33	1·0852	1·3758			

Specific Gravities and Refractive Indices of Aqueous Solutions of Chemically Pure Glycerin (*Strohmer*)

Glycerol. Per cent.	Sp. Gr. at 17·5° C.	Ref. Ind. at 17·5° C.	Glycerol. Per cent.	Sp. Gr. at 17·5° C.	Ref. Ind. at 17·5° C.	Glycerol. Per cent.	Sp. Gr. at 17·5° C.	Ref. Ind. at 17·5° C.
100	1·262	1·4727	83	1·218	1·4478	66	1·170	1·4206
99	1·259	1·4710	82	1·215	1·4461	65	1·167	1·4189
98	1·257	1·4698	81	1·213	1·4449	64	1·163	1·4167
97	1·254	1·4681	80	1·210	1·4432	63	1·160	1·4150
96	1·252	1·4670	79	1·207	1·4415	62	1·157	1·4133
95	1·249	1·4653	78	1·204	1·4398	61	1·154	1·4116
94	1·246	1·4636	77	1·202	1·4387	60	1·151	1·4099
93	1·244	1·4625	76	1·199	1·4370	59	1·149	1·4087
92	1·241	1·4608	75	1·196	1·4353	58	1·146	1·4070
91	1·239	1·4596	74	1·193	1·4336	57	1·144	1·4059
90	1·236	1·4579	73	1·190	1·4319	56	1·142	1·4048
89	1·238	1·4563	72	1·188	1·4308	55	1·140	1·4036
88	1·231	1·4551	71	1·185	1·4291	54	1·137	1·4019
87	1·228	1·4534	70	1·182	1·4274	53	1·135	1·4008
86	1·226	1·4523	69	1·179	1·4257	52	1·133	1·3997
85	1·223	1·4506	68	1·176	1·4240	51	1·130	1·3980
84	1·220	·4489	67	1·173	1·4223	50	1·128	1·3969

Specific Gravities and Refractive Indices of Aqueous Solutions of Chemically Pure Glycerin (*Skalweit*)

Glycerol. Per cent.	Sp. Gr. at 15° C.[1]	$n_{[D]}$ at 15° C.[2]	Glycerol. Per cent.	Sp. Gr. at 15° C.	$n_{[D]}$ at 15° C.	Glycerol. Per cent.	Sp. Gr. at 15° C.	$n_{[D]}$ at 15° C.
0	1·0000	1·3330	34	1·0858	1·3771	68	1·1799	1·4265
1	1·0024	1·3342	35	1·0885	1·3785	69	1·1827	1·4280
2	1·0048	1·3354	36	1·0912	1·3799	70	1·1855	1·4295
3	1·0072	1·3366	37	1·0939	1·3813	71	1·1882	1·4309
4	1·0096	1·3378	38	1·0966	1·3827	72	1·1909	1·4324
5	1·0120	1·3390	39	1·0993	1·3840	73	1·1936	1·4339
6	1·0144	1·3402	40	1·1020	1·3854	74	1·1963	1·4354
7	1·0168	1·3414	41	1·1047	1·3868	75	1·1990	1·4369
8	1·0192	1·3426	42	1·1074	1·3882	76	1·2017	1·4384
9	1·0216	1·3439	43	1·1101	1·3896	77	1·2044	1·4399
10	1·0240	1·3452	44	1·1128	1·3910	78	1·2071	1·4414
11	1·0265	1·3464	45	1·1155	1·3924	79	1·2098	1·4429
12	1·0290	1·3477	46	1·1182	1·3938	80	1·2125	1·4444
13	1·0315	1·3490	47	1·1209	1·3952	81	1·2152	1·4460
14	1·0340	1·3503	48	1·1236	1·3966	82	1·2179	1·4475
15	1·0365	1·3516	49	1·1263	1·3981	83	1·2206	1·4490
16	1·0390	1·3529	50	1·1290	1·3996	84	1·2233	1·4505
17	1·0415	1·3542	51	1·1318	1·4010	85	1·2260	1·4520
18	1·0440	1·3555	52	1·1346	1·4024	86	1·2287	1·4535
19	1·0465	1·3568	53	1·1374	1·4039	87	1·2314	1·4550
20	1·0490	1·3581	54	1·1402	1·4054	88	1·2341	1·4565
21	1·0516	1·3594	55	1·1430	1·4069	89	1·2368	1·4580
22	1·0542	1·3607	56	1·1458	1·4084	90	1·2395	1·4595
23	1·0568	1·3620	57	1·1486	1·4099	91	1·2421	1·4610
24	1·0594	1·3633	58	1·1514	1·4104	92	1·2447	1·4625
25	1·0620	1·3647	59	1·1542	1·4129	93	1·2473	1·4640
26	1·0646	1·3660	60	1·1570	1·4144	94	1·2499	1·4655
27	1·0672	1·3674	61	1·1599	1·4160	95	1·2525	1·4670
28	1·0698	1·3687	62	1·1628	1·4175	96	1·2550	1·4684
29	1·0724	1·3701	63	1·1657	1·4190	97	1·2575	1·4698
30	1·0750	1·3715	64	1·1686	1·4205	98	1·2600	1·4712
31	1·0777	1·3729	65	1·1715	1·4220	99	1·2625	1·4728
32	1·0804	1·3743	66	1·1743	1·4235	100	1·2650	1·4742
33	1·0831	1·3757	67	1·1771	1·4250			

It must be distinctly understood that the numbers given for the refractive indices hold good only for the stated temperatures. The variations due to changes of temperature may be gathered from the following table :—

Specific Gravity.	Variation of Refractive Index for 1° C.	Observer.
1·25350	0·00032	Listing.
1·24049	0·00025	Van der Willigen.
1·19286	0·00023	,,
1·16270	0·00022	,,
1·11463	0·00021	,,

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[1] Water at 15° C. = 1.

[2] $n_{[D]}$ is the refractive index for the sodium line D.

The variation in the case of pure water is 0·00008 for 1° C.

With a view to eliminating slight errors due to the adjustment of the instrument, *Lenz* recommends to take the refractive index of water immediately after the sample of glycerin has been examined, of course at the same temperature. Thus the numbers given in the following table were obtained :—

Differences between the Refractive Indices of Aqueous Solutions of Chemically Pure Glycerin and of Pure Water (Lenz)

Glycerol	$n_{[D]}$ Glycerol $- n_{[D]}$ Water.	Glycerol	$n_{[D]}$ Glycerol $- n_{[D]}$ Water.	Glycerol	$n_{[D]}$ Glycerol $- n_{[D]}$ Water.	Glycerol	$n_{[D]}$ Glycerol $- n_{[D]}$ Water.
Per cent.		Per cent.		Per cent.		Per cent.	
100	0·1424	74	0·1046	48	0·0645	22	0·0288
99	0·1410	73	0·1032	47	0·0630	21	0·0275
98	0·1395	72	0·1018	46	0·0616	20	0·0261
97	0·1381	71	0·1003	45	0·0601	19	0·0238
96	0·1366	70	0·0987	44	0·0587	18	0·0225
95	0·1352	69	0·0970	43	0·0572	17	0·0212
94	0·1337	68	0·0952	42	0·0556	16	0·0199
93	0·1323	67	0·0933	41	0·0541	15	0·0186
92	0·1308	66	0·0915	40	0·0526	14	0·0173
91	0·1294	65	0·0897	39	0·0510	13	0·0160
90	0·1279	64	0·0889	38	0·0495	12	0·0146
89	0·1264	63	0·0861	37	0·0479	11	0·0133
88	0·1250	62	0·0842	36	0·0464	10	0·0120
87	0·1235	61	0·0824	35	0·0451	9	0·0108
86	0·1221	60	0·0806	34	0·0438	8	0·0096
85	0·1206	59	0·0792	33	0·0424	7	0·0083
84	0·1191	58	0·0780	32	0·0411	6	0·0071
83	0·1177	57	0·0768	31	0·0398	5	0·0058
82	0·1162	56	0·0757	30	0·0385	4	0·0046
81	0·1148	55	0·0745	29	0·0372	3	0·0033
80	0·1133	54	0·0731	28	0·0358	2	0·0021
79	0·1119	53	0·0717	27	0·0345	1	0·0008
78	0·1104	52	0·0702	26	0·0332	0	0·0000
77	0·1090	51	0·0688	25	0·0318		
76	0·1075	50	0·0663	24	0·0315		
75	0·1061	49	0·0659	23	0·0302		

In the case of the dilute solutions of chemically pure glycerin, the numbers given in the preceding tables, as corresponding to the specific gravity and refractive index, indicate the percentage composition less accurately than do the methods described in Vol. I. Chap. VI.

Henkel and Roth[1] determined, therefore, the specific gravities of four gravimetrically prepared solutions of chemically pure glycerin (varying from 4·9905 to 19·3306 per cent of glycerol), and calculated with the aid of interpolation formulæ the numbers contained in the following table :—

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[1] *Zeits. f. angew. Chem.*, 1905, 1936.

Specific Gravities of Dilute Solutions of Chemically Pure Glycerin

Glycerol.	Specific Gravity at 15·4° C.	Specific Gravity at 20·4° C.	Specific Gravity at 25·4° C.
Per cent.			
1	1·00152	1·00059	0·99939
2	1·00398	1·00295	1·00172
3	1·00633	1·00532	1·00407
4	1·00877	1·00770	1·00642
5	1·01118	1·01009	1·00876
6	1·01359	1·01248	1·01115
7	1·01606	1·01488	1·01353
8	1·01851	1·01731	1·01591
9	1·02097	1·01973	1·01832
10	1·02344	1·02217	1·02073
11	1·02592	1·02462	1·02315
12	1·02841	1·02752	1·02559
13	1·03096	1·02593	1·02802
14	1·03341	1·03201	1·03047
15	1·03592	1·03449	1·03293
16	1·03844	1·03698	1·03540
17	1·04087	1·03948	1·03788
18	1·04351	1·04199	1·04037
19	1·04605	1·04451	1·04287
20	1·04861	1·04714	1·04638

In the case of samples of really chemically pure glycerin the oxidation methods should yield theoretical results, but if minute quantities of organic impurities have remained in the product, the percentage of glycerol will be found too high. This is shown by the following two analyses of a commercial "chemically pure" glycerin (*Lewkowitsch*[1]) :—

Comparison of the Acetin and Bichromate Methods

	Acetin Method.	Bichromate Method.
Chemically pure glycerin, specific gravity 1·2618.	99·04 ; 99·17	101·00 ; 101·9

In case the acetin method be resorted to, about 1 grm. of the substance is taken, and a somewhat larger excess of acetic anhydride than usual must be used in order to ensure complete esterification. *Grün and Wirth*[2] deduce the amount of water in pure glycerin from the depression of the boiling point. They record the following figures determined by *Schleiermacher's* method[2] :—

Glycerol. Per cent.	Boiling Point at 760 mm. °C.	Glycerol. Per cent.	Boiling Point at 760 mm. °C.
100	283-284	97	178-179
99·5	243-244	96·5	171-172
99	224-225	96	167-168
98·5	207-208	95·5	163-164
98	195-196	95	160-161
97·5	185-186		

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[1] *Analyst*, 1903, 105.

[2] *Zeits. f. angew. Chem.*, 1919, 32, 59-62.

Ash.—Theoretically, the proportion of ash should be *nil*, but as the last traces of metals cannot be removed from a product manufactured on a large scale, minute amounts of ash will always be found. The table given, p. 408, shows the ash ascertained in a number of commercial chemically pure glycerins. These numbers will afford guidance in judging as to whether in any given case the permissible maximum has been exceeded.

The ash may contain traces of sodium chloride. Lime and lead are not met with at present in chemically pure glycerins. The ash will chiefly contain copper or iron. The presence of iron is best ascertained by treating the glycerin with a dilute solution of tannin.

The German Pharmacopœia directs to test for iron by adding to the glycerin dissolved in four volumes of water a few drops of hydrochloric acid and of potassium ferrocyanide solution.

Organic Impurities.[1]—The presence of organic impurities is due to faulty manufacture. They may either consist of *acroleïn* and volatile fatty acids, such as *butyric acid*, or of substances having a higher boiling point than glycerol itself. The latter substances may be comprised under the name *polyglycerols*. Organic bases are not likely to be found in a chemically pure glycerin, as the taste alone would lead to the rejection of such glycerin.

The German Pharmacopœia prescribes the following test for esters of fatty acids: 50 c.c. of the glycerin diluted with 50 c.c. of water are heated on the water-bath for fifteen minutes with 10 c.c. of $\frac{N}{10}$ caustic potash. After cooling, the excess of potash is neutralised with $\frac{N}{10}$ hydrochloric acid, using phenolphthalein as indicator, when at least 4 c.c. of acid must be used.

A rapid "practical" test for volatile fatty acids is to spread a few drops of the sample on the back of the hand, and rub it gently into the skin. No smell of acroleïn or butyric acid should be then noticeable. A more reliable method is to mix the sample with alcohol and concentrated sulphuric acid, and heat it over a flame. In the presence of butyric acid the characteristic smell of ethyl butyrate, recalling that of pine-apples, will be noticed.

Acroleïn (as also any other reducing substance that may be present) is best detected by adding a few drops of a silver nitrate solution to an aqueous solution of the sample. No blackening or browning should appear after standing twenty-four hours at the ordinary temperature.

G. F. Bergh[2] is of the opinion that glycerol forms with acroleïn an acetal-like compound, which he terms glycerolacrylal.[3]

The German Pharmacopœia, edit. iii., prescribed the silver test in the following form:—Heat 1 c.c. of glycerin with 1 c.c. of ammonia to boiling, and add three drops of silver nitrate solution. No discoloration should be noticeable within five minutes. This test was originally intended to detect the presence of arsenic, but it is absolutely unreliable for this purpose. It is also worthless for the detection of other impurities, as so much depends on the mode of operating, that, on the one hand, an impure glycerin (one that has not even been distilled) may conform to the test, whereas, on the other hand, a pure glycerin is liable to be rejected. At the temperature of boiling water a mixture of glycerol and silver nitrate *does* become reduced at once after addition of ammonia (see Vol. I. Chap. III.). If, according to the directions of the Pharmacopœia, such an enormous excess of ammonia be mixed with glycerol, ebullition of the liquid may take place before the temperature of 100° C. is reached, and in that case the subsequently added silver nitrate will not be reduced.[1] This method must therefore be rejected.

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[1] Lewkowitsch, *Year-Book of Pharmacy*, 1890, 382.

[2] *Svenk. Farm. Tidsk.*, 1908, 385.

[3] Cp. Les Produits chimiques de Croissy, French patents 390,713, 392,978; English patent 16,528, 1908.

From these remarks it will be understood that the silver nitrate test can be made far more sensitive if a cold ammoniacal silver nitrate solution be used in place of neutral silver nitrate. Even the minutest traces of organic impurities, such as acroleïn or organic bases, are thus detected.

Acroleïn may be also detected by one of the tests described, Vol. I. Chap. III.

Sugar.—When glycerin is high in price adulteration with sugar (cane sugar or glucose) occurs. The presence of sugars is detected by polarimetric examination.

Polyglycerols[2] are detected and determined by allowing an accurately weighed quantity of the sample to evaporate gently at 160° C. Care should be taken not to heat too rapidly, otherwise even the purest glycerin may become polymerised with the production of the very substances that are to be detected. From the weight of the residue the weight of ash, subsequently found on incineration, must be deducted. The difference (the " organic residue ") is a fair indication of the care with which the glycerin has been manufactured.

The following table gives the " organic residue " and ash of a number of " chemically pure glycerins " examined in the author's laboratory;[2] they are arranged according to the amount of organic residue they contain :—

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[1] It may be mentioned that this Pharmacopœia test met with a strong protest on the part of a number of German glycerin manufacturers, who declared in a circular that they could not supply an article satisfying this test.

[2] Lewkowitsch, *Year-Book of Pharmacy*, 1890, 382.

[TABLE

Organic Residue and Ash in Commercial Chemically Pure Glycerins
(*Lewkowitsch*)

No.	Residue at 160° C.	Ash.	Organic Residue.
	Per cent.	Per cent.	Per cent.
1	0·03033	0·00603	0·0243
2	0·0276	0·00300	0·0246
3	0·0377	0·005	0·0327
4	0·0498	0·0138	0·0360
5	0·0452	0·0081	0·0371
6	0·0509	0·0066	0·0443
7	0·0656	0·0139	0·0517
8	0·0748	0·0140	0·0738
9	0·0905	0·0154	0·0751
10	0·1047	0·0190	0·0857
11	0·1236	0·0305	0·0931
12	0·1621	0·0183	0·1438
13	0·8060	0·2090	0·5970

Rules for the valuation of commercial chemically pure glycerins may be derived from this table. The first six samples certainly deserve the name of chemically pure glycerin, the following four samples represent lower qualities unfit for pharmaceutical purposes, whereas the last two samples are merely glycerins refined by distillation; the last sample would be rejected as unsuitable even by dynamite makers.

Sample No. 2 represents chemically pure glycerin manufactured by the author on a large scale from soap-lye glycerin.

One of the most important tests in the examination of chemically pure glycerin is the test for **Arsenic.**

This metal should be wholly absent. It should be borne in mind that if once arsenic has found its way into glycerin, it cannot be removed by the usual processes of refining,[1] as glycyl arsenite, $AsO_3(C_3H_5)$, the substance formed when arsenious acid is dissolved in glycerin, distils over with the latter (Vol. I. Chap. III.). Hence many commercial brands are contaminated with arsenic, some to such an extent that they are decidedly harmful when used for medicinal preparations, or otherwise taken internally.

A rapid and extremely sensitive test for arsenic is *Gutzeit's* test :—

Place 2 c.c. of the sample in a high test-tube, add some zinc, free from arsenic, and a few c.c. of pure dilute sulphuric acid. The test-tube is then covered with a tightly fitting cap of filter paper, two or three layers thick, the innermost layer having been previously moistened, by the aid of a glass rod, with a 50 per cent solution of silver nitrate. In presence of arsenic arseniuretted hydrogen is given off. After ten minutes' standing the paper cap is taken off and examined. No deep yellow stain must be noticeable on the inner fold; only a slight yellowish coloration may be permissible. The yellow compound formed if arsenic be present consists, as *Poleck and Thümmel*[1] have shown, of the double salt $AsAg_3(AgNO_3)_3$. This salt is decomposed by three molecules of water into $As(OH)_3 + 3HNO_3 + 6Ag$. Hence the yellow stain rapidly disappears, if moisture be present, or even if too much water vapour be developed from the test solution, in which case the paper cap becomes black through separation of metallic silver. It is not advisable to use hydrochloric acid, as, if the solution becomes too hot and is too concentrated, hydrochloric acid gas may be given off, when the formation of silver chloride masks the yellow colour. *Poleck and Thümmel* give as the limit of sensitiveness 0·005 mg. As_2O_3, *Beckurts*[2] gives 0·002 mg. As_2O_3. *Flückiger* estimates that a stain appears if arsenious acid be present only to the extent of 0·001 to 0·0001 mg. (In *Marsh's* apparatus even smaller quantities of arsenic can be discovered, but such accuracy is usually not required in the examination of glycerin.[3])

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[1] Lewkowitsch, *Year-Book of Pharmacy*, 1890, 380.

This test is so extremely sensitive that it is absolutely necessary to make a blank test side by side with it, using the same reagents. The silver nitrate test is almost too delicate (although there are commercial glycerins which will not show any coloration after ten minutes) and has therefore been replaced by a less rigorous one, in which a concentrated solution of mercury bichloride is substituted for silver nitrate. A glycerin is considered as practically free from arsenic if no yellow coloration appear after ten minutes. If mercury bichloride be used, hydrochloric acid may be employed instead of sulphuric acid.

The composition of the yellow body formed in this reaction was found by *Franceschi*[4] to be $AsH(HgCl_2)$. The substitution of mercuric chloride for silver nitrate was first proposed by *Merceron and Bergeret.*[5] *Flückiger*[6] gives as the limit of sensitiveness 0·002 mg. As_2O_3.

It should, however, be noted that the sulphuretted hydrogen, which is evolved if sulphides be present, also produces a yellow stain. In order to exclude errors, sulphides must be oxidised first to sulphates (with permanganate solution, potassium, chlorate, or iodine). The author tested for presence of sulphides by proceeding as in *Gutzeit's* test, but substituting a paper cap moistened with lead acetate instead of silver nitrate ; a black stain points to the presence of sulphides. With a view to detecting sulphides and arsenic in one and the same sample, it has been proposed to pass the gas evolved through a solution of lead acetate before it comes into contact with the paper cap. As this method involves the use of cumbersome apparatus, it has been suggested to conduct the gas over paper, moistened with lead acetate (*Dowzard*[7]) and then dried (*Hill and Collins* [1]), whereby sulphuretted hydrogen is retained.

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[1] *Arch. der Pharm.*, 222 (1884), p. 19.

[2] *Jahrb. der Pharm.*, 1883, 475.

[3] With regard to the use of the Marsh apparatus, cp. "Detection and Determination of Arsenic." Reprinted from the *Journal of the Society of Chemical Industry*, Eyre and Spottiswoode, London, 1901 ; cp. also Gotthelf, *Journ. Soc. Chem. Ind.*, 1903, 191 ; Goode and Perkin, *Journ. Soc. Chem. Ind.*, 1906, 507 ; G. Lockemann, *Zeits. f. angew. Chem.*, 1905, 416 ; *Journ. Soc. Chem. Ind.*, 1907, 1115.

[4] L'Orosi, 13, 289

[5] *Compt. rend.*, 1874 (79), 118.

[6] *Arch. d. Pharm.*, 1889 (27), 1.

[7] *Chemist and Druggist*, 1900, 478.

If the arsenic be present in the higher state of oxidation (as arsenate), a somewhat prolonged time (*Bird* [2]) is required for the reduction to arseniuretted hydrogen ; in order to accelerate the reduction, some stannous chloride solution (free from arsenic) may be added to the sample.[1]

The bulk of chemically pure glycerin is used in pharmaceutical practice, and for keeping tobacco (snuff) moist. It is further employed for preserving meat and fruits, and also in the maceration process for extracting delicate perfumes from flowers. Its use in the brewing and wine industries may also be mentioned.

A careful estimate made by the author would lead to the conclusion that the quantity of soap-lye crude made in this country amounts to approximately 25,000 tons per annum. To this should be added the crude glycerin obtained in the candle industry, which is estimated to amount to about 500 to 600 tons per annum. For statistical data as to imports into, and exports from, this country see pp. 6-18.

The quantity of soap crude glycerin made in the United States may be taken to amount to about 13,000 tons per annum. From the candle industry there are obtained a further 4000 tons, leading to about 16,000 to 17,000 tons of crude glycerin produced in the States. The import of crude glycerin from Europe approximated to 17,000 tons in 1907 (and 15,000 tons in 1906). In 1909, 20,000 tons were imported, and in 1911 and 1912, 17,300 tons and 12,700 tons respectively.

The official statistics given for Germany are collated in the following table :—

Imports into, and Exports from, Germany of Crude Glycerin [3]

	Imports.	Exports.
	Metric tons.	Metric tons.
1905	4952	584
1906	3529	2136
1907	2947	2142
1908	5375	1292
1909	3530	1580
1910	4685	1686
1911	5148	2416
1912	5875	2316
1913	5374	2237
1920	1017	256

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[1] *Chemist and Druggist*, 1905, 548.

[2] *Analyst*, 1901, 181.

[3] In addition to this—

	Soap Lyes. Imports. tons.	Soap Lyes. Exports. tons.
1908	4775	14
1909	5682	50

Imports into, and Exports from, Germany of Distilled Glycerin

	Imports.	Exports.
	Metric tons.	Metric tons.
1905	713	3513
1906	668	2324
1907	786	1743
1908	721	2108
1909	680	2354
1910	914	2594
1911	1241	2403
1912	1188	3751
1913	1107	3937
1920	186	...

II. Technology of Waxes

At present the technology of waxes has not the same commercial importance as that of the natural oils and fats, inasmuch as the quantity of the waxes furnished by plants and animals is much more restricted than that of oils and fats; it would, however, appear that with the extension of bee-keeping as a house industry, the supplies of beeswax could be easily increased. Wool wax also could be readily obtained in much larger quantities than has been the case hitherto, if a more remunerative use than the present one could be found for it. Vegetable waxes, although very widely distributed in nature, occur in such small quantities that their recovery, if practised as the chief industry, must remain expensive, but it may become feasible to obtain in large quantities as by-products such waxes as Rhimba and sugar-cane wax, especially the latter, as the enormous quantities of sugar cane worked up in tropical countries would appear to furnish the material for this hitherto neglected product.

On account of the restricted quantities that are available, the prices of waxes are very much higher than those of oils and fats. As the alcoholic constituents[1] of the known waxes are not yet obtainable from any other source, the *synthetical* preparation of waxes cannot yet be looked upon as a problem that is likely to be realised in the near future. The few waxes that have been prepared synthetically have been enumerated in Vol. I. Chap. I.

As waxes are not digestible, their preparation for *edible* purposes cannot be entertained.

The chief uses to which the natural waxes are put have been detailed already in Vol. II. pp. 872-947. It is therefore only necessary to supplement the remarks made there by some further notes.

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[1] For a "vaseline-like" preparation, stated to be made from the higher alcohols occurring in spermaceti, and sold under the fancy name "cetosan," cp. F. Blatz, *Pharm. Zentralh.*, 1908, 537.

The *liquid* waxes are chiefly used as lubricating oils (see Chap. XV.); their technology and examination has been considered already at length (Vol. II. pp. 872-880). For oxidised oils from liquid waxes, cp. p. 189.

The *solid* waxes are used in their original state, or at most after a simple preliminary purification by remelting, for the manufacture of candles, polishes, insulating compounds, plastic masses, phonograph masses, emulsions, modelling wax, and in pharmaceutical practice for the preparation of cerates, salves, ointments, etc.

The saponification of waxes [1] is not carried out on a commercial scale. The attempts to saponify wool fat by means of lime in an autoclave (*Buisine* [2]), or by other agencies,[3] and to prepare a soap from wool fat have not proved successful, and the industry connected with the working up of wool fat must still be classed with those considered under "Waste Waxes" (see Chap. XVI. p. 448).

WAX CANDLES

(*a*) *Sperm Candles*

Sperm candles are made from refined spermaceti. They are at present still used for illuminating, but have been almost completely ousted by the cheaper stearine and paraffin candles. Until recently sperm candles were employed as the standard for photometrical measurements by gas examiners in this country, and are still in use for this purpose.

Spermaceti alone cannot be employed for candles, as the material is too brittle. The rules for the preparation of standard sperm candles for photometrical purposes, published by the Metropolitan Gas Referees,[4] prescribe that for the purpose of rendering spermaceti less brittle, best air-bleached beeswax, melting at, or about, 144° F. (62° C.), shall be used (and no other material), and that the proportion of beeswax to spermaceti shall not be less than 3 per cent, nor more than 4·5 per cent. The spermaceti itself shall be so refined as to have a melting point lying between 112° F. and 115° F. (45°-46° C.). The melting point is to be determined as follows:—

"A small portion of the spermaceti is melted by being placed in a short test-tube, the lower end of which is then plunged in hot water. A glass tube drawn out at one end into a capillary tube about 1 mm. in diameter is dipped, narrow end downwards, into the liquid spermaceti, so that when the tube is withdrawn 2 or 3 mm. of its length are filled with spermaceti, which immediately solidifies. The corresponding part of the exterior of the tube is also coated with spermaceti, which must be removed. The narrow part of the tube is then immersed in a large vessel of water at a temperature not exceeding 100° F. (37·8° C.). The lower end of the tube, which contains the spermaceti, should be three or four inches below the surface and close to the bulb of a thermometer. The upper end of the tube must be above the surface and the interior of the tube must contain no water. The water is then slowly heated, being at the same time briskly stirred, so that the temperature of the whole bulk is as uniform as possible. When the plug of spermaceti in the tube melts it will be forced up the tube by the pressure of the water. The temperature at the moment when this movement is observed is the melting point."

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[1] Montanwax (p. 291) may be considered as obtained by hydrolysis of a natural vegetable wax occurring in (or representing) lignite bitumen.

[2] Cp. German patent 32,015, Violette, Buisine and Vinchon (*Norddeutsche Wollkämmerei und Kammgarnspinnerei*), and German patent 99,502 (C. Schmidt); German patent 134,183 (Hopkinson, Cowley, and Illingworth).

[3] German patent 55,110.

[4] *Journ. Soc. Chem. Ind.*, 1894, 65.

Spermaceti candles, like stearine candles, can be moulded in candle machines.

(*b*) *Beeswax Candles*

Beeswax candles are, as a rule, not moulded like the candles described, p. 295, as they adhere strongly to the moulds of the candle machine; even if they are detached from them, they lose their shape, or crack (cp. below). The tapers and thicker cables of beeswax are made by "drawing," *i.e.* pulling a wick by means of simple machinery through the melted wax, and then through a die until the cable has acquired the desired thickness. Large wax candles are made by "pouring" melted beeswax at a suitable temperature on to a wick hanging vertically from a hoop. When the layer has cooled, fresh layers of wax are poured on to it until the candle has reached the desired thickness. The candles are then rolled on a marble slab under a board until they assume the desired length.[1] Finally, an even surface is given by dipping the candles in melted wax at a somewhat high temperature. Beeswax candles, therefore, show concentric layers, which can be easily peeled off, if necessary, for separate examination. In order to render the beeswax plastic and prevent the cables or candles from sticking, a small quantity of oil of turpentine is added (Vol. II. p. 909).

The thickness of the wick, and the preparation of it for the candle, requires great circumspection. Twisted or plaited wicks are now supplied to the trade by special works. The "pickling" of the wick is done in a manner similar to that employed in the manufacture of stearine or mixed stearine and paraffin candles (see p. 296). The solutions chiefly in use are composed of ammonium salts containing boric acid and a small amount of a bismuth salt.

Recently a machine has been constructed for producing beeswax candles by "dipping"; it is claimed that the output is much larger than can be obtained by the methods described above.[2] The processes of decorating and painting beeswax candles fall outside the scope of this work. It may, however, be pointed out that coloured candles may require to be examined for poisonous metals.

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[1] Baenar, German patent 234,059.

[2] J. Kirchens, German patent 170,155; cp. German patent 212,896 (J. Karl). A special contrivance for ascertaining the weight of a candle whilst it is in course of manufacture is patented by J. Kirchens (German patent 160,418).

Yellow beeswax candles are largely used for ritual purposes, but as they are apt to burn with a smoky flame, bleached beeswax is preferred.

The candles burned in Greek Catholic churches must consist of pure beeswax. The wax for such candles, if white, is air-bleached, as chemically bleached wax yields a candle of a coarse and crystalline texture (" grain "), which does not burn satisfactorily. The Roman Catholic Church formerly required the candles to be made of pure beeswax; recently, however, the admixture of a certain amount of other candle materials has been permitted. The candles made for ritual purposes in this country contain 75, 65, and 25 per cent, respectively, of pure beeswax; the percentage of pure beeswax is stamped on them. In such candles the coarse grain of chemically bleached wax is obliterated (cp. Vol. II. p. 908). On the Continent " church-wax candles " are sold which frequently contain no true beeswax whatever, but consist for the most part of stearine, paraffin wax, no more than 10 per cent of ceresin, and about 5 per cent of carnaüba wax. The examination of beeswax candles for the true amount of beeswax has therefore assumed considerable importance.

The examination of the material is carried out in a manner identical with that described under the examination of beeswax; the reader must therefore be referred to Vol. II. pp. 919-939. It may, however, be added that beeswax intended for candle-making is not mixed with any considerable quantity of Japan wax and carnaüba wax, as these ingredients, if present to a large extent, render a beeswax candle practically useless. Hence candles which contain considerable quantities of carnaüba wax are free from beeswax. Thus a candle, represented to be a beeswax candle, gave on analysis the following results :—

Carnaüba wax . . .	60 per cent.
" Stearine " . . .	25 ,,
Ceresin	15 ,,

It should, however, be pointed out that candles shipped to hot climates are now admixed (" hardened ") with 5 to 10 per cent of white (bleached) carnaüba wax or of montanwax, or they are " cased " with these materials by dipping. In the United States " beeswax " candles are made which contain a notable amount of myrtle wax.

Moulded " beeswax " candles are made from a mixture of bleached beeswax and spermaceti. In order to prevent the sticking of the candles to the tinned moulds, the insides of the latter are generally rubbed over with a little oil.

Wax " vestas " consist chiefly of paraffin wax, mixed with a little stearine in order to render them opaque; they are frequently " stiffened " by the addition of montanwax or bleached carnaüba wax.

Modelling Waxes.—These usually consist of beeswax, or mixtures of beeswax and Japan wax, and copal. They are frequently filled with talcum. Sometimes castor oil and glycerin are added, and the talcum may be substituted by sulphur or pipe-clay.

Phonograph Masses.—These consist of mixtures of stearic acid, carnaüba wax, montanwax, ceresin, etc., to which a colouring matter like lamp-black is added. The addition of aluminium stearate has been patented.[1] Mixtures to which rosin or asphalt have been added have been patented by *Winter and Winkler*.[2]

WAX POLISHES

The best wax polishes (for leather, linoleum, furniture, etc.) are made by dissolving beeswax in oil of turpentine in the hot. The proportions of beeswax and solvent are varied according to the desired consistence. These polishes are frequently coloured and even perfumed. Cheaper polishes are manufactured by substituting paraffin wax (or ceresin) for beeswax; in order to restore the hardness lost through the admixture of softer material, carnaüba wax or montanwax is added. The oil of turpentine is (in the United States) mostly substituted by "long leaf pine oil" and by "wood oil" (see p. 171); it is also frequently substituted by petroleum hydrocarbons, etc. (cp. p. 172). Inferior polishes contain no beeswax at all; they consist frequently of carnaüba wax, ceresin, montanwax, paraffin wax, stearine, and fish oil.[3]

Whereas the polishes described above contain little or no water, *polishing creams* are made by treating beeswax with solutions of carbonate of potash in the hot, whereby the whole or part of the free acids is converted into soap, which emulsifies the neutral part of the wax. These emulsions are capable of "holding" considerable amounts of oil of turpentine, which is generally intermixed with the best kinds of this class of polishes. Frequently hard soap is added. Lower kinds of "creams," such as *floor polishes* or solutions used for coating ("sizing") paper, do not contain any oil of turpentine.

Boot polishes are made in a similar manner from beeswax or carnaüba wax, montanwax, candelilla wax, etc. The inferior kinds contain considerable quantities of stearine, paraffin wax,[4] montanwax, and even rosin, etc. The preparation of polishes from the juices of plants of the Euphorbiacea species in admixture with stearine or ceresin has been patented [5] (cp. Vol. II.). The addition of yolk of egg and egg oil has been patented.[6]

Wax varnishes are mixtures of beeswax with linseed oil (raw or "boiled") with or without oil of turpentine.[7]

Methods of analysing wax polishes and wax varnishes must be adapted to each special case; the directions given for the examination of beeswax (Vol. II. pp. 919-939), lubricating greases (p. 72), and varnishes (p. 159) must be suitably combined for this purpose.

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[1] New Jersey Patent Co., English patent 3070, 1905; German patent 223,276.
[2] German patent 227,208.
[3] Kuki Ges., vorm. C. Mähler und Cie, German patent 244,089.
[4] Cp. H. Schäfer, German patent 229,423.
[5] Baumeister, German patent 258,259.
[6] Johannsson and Co., German patent 234,728.
[7] For vulcanised (bitumen acid) waxes cp. English patent 21,742, 1907 (S. Paterson).

WAX EMULSIONS

Waxes possess the power of emulsifying considerable quantities of water. This property is made use of in pharmaceutical practice for the production of pomades, salves, etc., all of which may be looked upon as solid emulsions (just as solid lubricants were considered above as representing solid emulsions). Wool grease and wool wax possess the property of forming emulsions to the most notable extent. In the wash waters from woollen mills the wool grease forms so persistent an emulsion with the water that it is impossible to separate the whole of the wool fat by a cream-separator such as would readily remove the fat from milk. This ready emulsifying power is made use of by curriers (in currying leather), further in the preparation of salves from wool wax (lanolin), and from the constituents into which wool wax can be resolved (" lanogenes ") (see Chap. XVI. " Waste Waxes "), and lithographic inks.[1] Beeswax gives an emulsion, which is very persistent, with a 1 to 5 per cent solution of borax. Spermaceti does not show this behaviour.[2] The following table, due to *Dieterich*, supplies some numerical data regarding the emulsifying power of lanolin compared with other substances :—

100 Parts of	Give a complete Emulsion with Parts of water.
Lanolin	105
Mixture of 80 parts of lanolin and 20 parts of olive oil	320
Mixtures of 20 parts of white beeswax and 80 parts of oleic acid	228
Butter fat	165
Lard	15
Paraffin wax	4

For the preparation of emulsions made from waxes (beeswax, carnaüba wax, wool fat) with mineral oils, cp. the patent specifications of *Urbanek*,[3] *Wallbaum*,[4] *Knopf*,[5] and *Th. Svedberg*.[6]

Montanwax, see above, p. 291.

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[1] French patent 397,923 (Manche, Noclain et Chavet).

[2] Pinkus, *Chem. Zeit.*, 1910, 278.

[3] German patent 159,526.

[4] English patent 4116, 1906.

[5] English patent, 17,523, 1907.

[6] French patent 403,592.

CHAPTER XVI

TECHNOLOGY OF WASTE OILS, FATS, AND WAXES, AND THE COMMERCIAL PRODUCTS DERIVED THEREFROM

1. Waste Oils and Fats

A. FOOTS FROM REFINING VEGETABLE OILS AND FATS

In the course of refining *linseed oil*, *rape oil*, and the lowest kinds of *olive pulp oils* by means of sulphuric acid, black tarry masses—" foots " —(French, " *Crasses* " ; German, " *Ölsatz*," " *Öltrub*," " *Sauertrub* ") are obtained, which contain, besides carbonised organic matter, remnants of oil and of fatty acids. These latter substances are to some extent mechanically intermixed with the carbonised residue, but are chiefly held in solution owing to the strong solvent power of the sulphonated oils and fatty acids.

In most linseed oil refineries these residues used to be thrown away, as mere boiling up with water did not lead to the liberation of the entangled oil. Owing to the stringent rules of sanitary authorities, these residues, even if highly diluted with water, must no longer be run into sewers. The crudest way of disposing of these residues is to mix them with sawdust and burn the mass as fuel. A more rational use is to employ them in the manufacture of shoe-blacking and printing-ink.[1] For the working up of the foots from *rape oil* see Vol. II. p. 263 ; for those from *olive oil* see Vol. II. p. 353, and Vol. III. pp. 118, 207.

Of much greater value are the foots obtained in the preparation of *vegetable butters* (see Chap. XV. p. 56).

These foots, consisting as they do of a mixture of soap and neutral fat, are generally decomposed with sulphuric acid, and the resulting mixture of neutral fat and fatty acids is sold for soap-making purposes.

The examination embraces the determination of free fatty acids and neutral fats. The detection and determination of mineral acids and of ash (soda, lime, etc.) should not be omitted, as they frequently contain considerable quantities of lime soaps or lime not removed thoroughly.

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[1] British Oil and Cake Mills and A. G. Wass, English patent 23,231, 1900.

COTTON SEED FOOTS

On refining cotton seed oil by means of caustic soda (Vol. II. p. 202) a precipitate is obtained which consists of a mixture of cotton seed oil soap, neutral cotton seed oil,and colouring and resinous matters. The precipitate is known in this country under the trade term " mucilage," and in the United States of America as " soap stock."

In the latter country the working up of these foots has assumed very considerable commercial importance, as the quantity produced in the United States is estimated to amount annually to approximately 432,000 barrels (of about 40 gallons each), having the value of about 1,500,000 dollars.[1]

American cotton seed foots are worked up for *cotton seed foots soap* (foots soap) and (or) for *black grease.*

Cotton Seed Foots Soap.—According to the quality and the age of the cotton seed worked up for oil, the strength of the caustic lye employed, and other conditions affecting the quality of the oil, the colour of the " soap stock " varies from light dirty yellow through dark green to deep red. On exposure to the air the soap stock becomes black. Its consistence also varies with the conditions enumerated above, and, in addition to this, with the care and skill exercised by the refiner. Hence the specific gravity of the soap stock varies from 0·97 to 1·04, and the percentage of fatty acids fluctuates between 35 and 60. The " soap stock " is sold on the basis of 50 per cent fatty acids ; its average composition is as follows :—

Fatty anhydrides	48·50	per cent.
Glycerin	3·98	,,
Caustic soda, as Na_2O	3·20	,,
Foreign organic matter	5·90	,,
Colouring matter	2·42	,,
Water	36·00	,,
	100·00	

Wagner and Clement[2] publish the following analysis of an imported soap stock :—

Water	32·4	per cent.
Fatty acid as soap	38·7	,,
Neutral oil + Unsaponifiable	23·5	,,

German soap stock from Egyptian seeds :—

Water	42·67	34·35
Mineral matter	10·52	8·34
Neutral oil	8·25	22·79
Fatty acids	34·56	33·18
Unsaponifiable	2·30	1·91

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[1] D. Wesson, *Journ. Soc. Chem. Ind.*, 1907, 595.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909 (xvii.), 266.

As will be seen, the unsaponifiable matter (crude phytosterol) accumulates in the soap stock.

The author found 49 and 51 per cent of total fatty matter in cotton seed soap stock, together with 0·8 and 0·99 per cent of a whitish resinous matter insoluble in ether and in caustic soda.

The 48·5 per cent of fatty anhydrides in the above given analysis correspond to a "50 per cent soap stock." The *Inter-state Cotton Seed Crushers' Association* of the United States prescribe the following official method for the determination of the total fatty acids in soap stock: 8-10 grms. are weighed out and saponified with alcoholic soda solution. The alcohol is driven off and the soap washed out into a beaker with 400 c.c. of hot distilled water. When the soap is dissolved the solution is acidified with dilute sulphuric acid and heated until the layer of fatty acids is quite clear. These are then allowed to solidify, the acid liquor poured off through a filter and the cake washed free from sulphuric acid, and allowed to dry over-night in a desiccator. The fatty acids are placed in a folded filter and extracted in a Soxhlet with gasoline for three hours. The beaker is washed with the gasoline which is added to the bulk. The gasoline is distilled off and the fatty acids dried to constant weight.[1]

Soap stock containing more than 40 per cent of water ferments readily; therefore the refiners, who do not work up the stock themselves for commercial soap, deliver it to soapmakers in the freshest possible condition. In the soapery the soap stock is boiled up with a small excess of caustic soda and then salted out. The dark lye, which contains most of the impurities and foreign organic substances, is run to waste. The "curd," known as "killed foots," is washed repeatedly with alkaline lyes, and treated as described under "Soap Manufacture" (p. 317), when finally a dark yellow to brown soap results. The freshly made soap contains approximately 63 per cent of fatty acids. As its consistence is somewhat soft, it is allowed to dry in the works until it contains about 66 per cent or more of fatty acids. This is one of the cheapest soaps made in the United States, and is used there largely in the manufacture of low-class soap powders and washing powders (cp. p. 352).

Cotton seed oil being a semi-drying oil, its fatty acids are somewhat readily oxidisable, and hence explosions of soap powder made from "soap stock" must be guarded against (see Chap. XV. p. 352).

A patent for the recovery of a substitute for shellac from cotton seed foots has been taken out by *Loeschigk*,[2] who oxidises the alkali soap solutions with hydrogen peroxide which converts the bodies of a non-fatty nature into a rosin-like mass. These are precipitated together with the fatty acids by means of dilute mineral acids, and the fatty acids extracted from the mixture by means of volatile solvents.

Enormous quantities of this soap were sent to this country, and found extensive use, on account of the low price, in some woollen and union goods mills as textile soap, although the employment of such soap is distinctly injurious to the goods. But owing to the erection of distillation plants in the United States the " soap stock " is now worked up in the United States for oleine and stearine.

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[1] Cp. Stiepel, *Seifensieder Zeit.*, 1909, 1223, and Smalley, *Journ. Ind. Eng. Chem.*, 1912, 893.

[2] German patent 220,582; cp. also Stiepel, German patent 219,716.

Black Grease.—When " soap stock " cannot be worked up readily into soap, nor sold in the fresh state (for a fermented soap stock yields a very dark soap), it is treated with sulphuric acid in the hot, when the fatty matter rises to the top as a black mass, known in commerce as *black grease.* Most of the black grease obtained in the United States is shipped to this country to be worked up as described below. Endeavours are, however, being made at present to establish the distillation in the United States.

Egyptian seed, which is crushed chiefly in this country and on the Continent of Europe, usually " heats " during the voyage and when stored. In consequence of the changes which the seed has undergone, the crude cotton seed oil has a much darker colour than American crude oil, and the " foots " obtained from it are almost black.

Experiments made on a large scale to prepare a saleable soap from foots obtained from Egyptian seed have failed hitherto ; hence such foots are solely worked up for " black grease."

Black grease is sold on the basis of the " fatty acids " it yields. The method of ascertaining the amount of valuable fatty acids is usually agreed upon between buyer and seller, as the fatty acids separated in the usual manner after saponifying the grease contain resinous matters, so that the customary calculation to oleic acid gives too high results. Where no such stipulations exist, it is usual to calculate the total fatty acids to oleic acid, as was done in the case of the analysis set out in the following table :—

Analysis of Black Grease (*Lewkowitsch*)

	From American Cotton Seed.			From Egyptian Cotton Seed.
	I.	II.	III.	
	Per cent.	Per cent.	Per cent.	Per cent.
Total fatty acids calculated to oleic	89·1	88·3	91·64	92·6
Free fatty acids calculated to oleic .	50·11	...	...	...
Volatile fatty acids calculated to mean molecular weight 150 . .	...	0·28	...	...
Unsaponifiable matter . . .	...	5·95	...	...
Saponification value . . .	...	194·1	...	...

On a large scale the " black grease " is subjected, after a suitable preliminary treatment, to distillation in a current of super-heated steam, much in the same manner as the distillation of fatty acids is carried out in candle works (Chap. XV. p. 238).

The distillate thus obtained consists chiefly of free fatty acids, and is worked up in the same manner as is done in the case of the distilled fatty acids of candle works. Thus "oleine" and "stearine" are prepared. The latter is frequently termed in commerce "cotton seed stearine," and must not be confounded with the true cotton seed stearine (vegetable margarine), described Vol. II. p. 204. The still residue is sold as "cotton pitch," or "cotton oil pitch," or "cotton stearine pitch."

In the following table are given the analyses of a set of samples obtained on a commercial scale from a "run" made with a "black grease," the composition of which is indicated in the first horizontal line.

Examination of a Black Grease and the Products derived therefrom (Lewkowitsch)

	Titer Test.		Acid Value.	Saponification Value.
	°C.	°F.		
Black Grease	...	...	110·6	163
Distilled Grease	...	...	186·6	189·3
"Oleine"	...	...	169·1	173·5
Pressed Stearine Cake	...	...	204·6	205·3
Redistilled Oleine	...	...	156·2	183·2
"White Grease" No. 1	42·0	107·5	196·9	198·2
"White Grease" No. 2	43·05	109·5	201·1	202·0
"White Grease" No. 3	44·8	113·0	193·4	196·7
White Stearine	51·2	124	191·5	192·2

The amount of "unsaponifiable matter" in the distilled products depends to a very large extent on the skill of the operator in conducting the preliminary purification and the distillation of the crude material.

"Oleine" and "stearine" are used in the manufacture of low-class soaps, provided their content of unsaponifiable matter be low; otherwise they are employed as "wool oils" and in the manufacture of sizes, lubricating greases, etc. If the melting point of the "stearine" be high, it can serve as candle material of an inferior quality. Samples of stearine so used gave the following numbers on examination in the author's laboratory:—

	I.	II.
Solidifying Point	45·6° C.	42·5° C.
Iodine Value	54·9	...
Unsaponifiable Matter	5·2 per cent	...
Acid Value	...	198·6

B. WASTE ANIMAL FATS

1. Greases

Under this head fall all fats obtained from refuse material, such as kitchen grease ("melted stuff"), ship's grease ("Schiffssparfett"), tripe tallow, slaughter-house grease ("tankage" grease), bone grease, skin grease, greases from carcase-rendering establishments, "animal grease," "animal oil," etc. These greases must be looked upon as varieties of lard, tallow, bone fat, horse fat, etc. The chemical examination of these greases embraces the determination of the amounts of dirt and water, free fatty acids, and unsaponifiable matter.

(*a*) Slaughter-house Greases

French—*Petits suifs*; *graisses d'abattoirs.* German—*Schlachthausfette.*

The recovery of greases from slaughtered animals has assumed the dimensions of a large and properly conducted industry since the very primitive slaughter-houses, with their extremely insanitary conditions and their great waste of valuable material, have given way to large establishments, which are worked as adjuncts to the modern slaughter-houses. The immense packing-houses of the United States, in which the main attention is directed to the economical use of every scrap of meat and of all the by-products, have served as models to the European establishments. Under the pressure of the various Boards of Health, who issued stringent rules regarding the disposal of objectionable refuse-products, the slaughter-houses, at any rate in the large towns, can now be well compared with chemical works constructed on most modern lines. Under the heading "Lard" (Vol. II. Chap. XIV. p. 699), there has been given already an outline of the mode of working as carried out in packing-houses. This need only be supplemented here by indicating the method of working up "tankage," and of recovering the different qualities of greases.

All the waste meat, scrap, etc., is collected in large digesters [1] (autoclaves), mixed therein with water, and treated with steam under high pressure [2] (so as to avoid the escape of noxious, or evil-smelling gases). After the material has been well disintegrated ("cooked"), the contents are allowed to settle, when the fat which was imprisoned in the meat cells (tallow or lard, or a mixture thereof, according to the raw material) settles out as an upper layer. The "grease" is withdrawn into suitable receptacles when it is ready for use in the soap, candle, and other industries. The remaining contents of the digesters are run into large "tanks" underneath, where a further quantity of "grease" separates on the top of the aqueous gluey liquor ("soup"), whereas the disintegrated fibres of meat, etc., fall to the bottom. The separated grease

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[1] Gibaud and Baug, French patent 462,278; Rosenkranz, German patent 259,966.

[2] Meyer, German patent 232,933.

(" skimmings ") is skimmed off and added to the next charge of " tankage," whilst the aqueous liquor is drawn[1] off and concentrated in vacuum evaporators[2] to a syrupy liquid (" concentrated tankage," " stick "). The solid matter in the tanks still contains a considerable amount of grease, which is recovered by subjecting the whole mass to pressure in hydraulic presses, when water and grease run out; the latter is added to the next charge of " tankage," together with the " skimmings." The following analyses due to *Wright* show the composition of dried tankage :—

	1.	2.	3.
Moisture, per cent	10·62	8·24	6·20
Tricalcic phosphate, per cent	23·94	11·60	12·12
Nitrogen, per cent	7·50	10·16	10·08
Fat, per cent	15·32	14·40	15·96

The mass left in the press-cloths is worked up for " fertiliser " by transferring it to mechanical (intermittent or continuous) dryers (cp. Vol. II. " Menhaden Oil "), in which the material is dried until it contains less than 10 per cent of moisture.[3] It is sold on the basis of phosphate and ammonia which it contains. (Thus 7/30 tankage is meant to signify a tankage containing 7 per cent of ammonia and 30 per cent of phosphoric acid.)

In many establishments it is usual to mix the " stick " with the hydraulically expressed material in the drying machine.

In large establishments, lard greases and tallow greases can be recovered separately; in smaller slaughter-houses the products are generally mixed on account of the necessity for the rapid disposal of the objectionable raw material.

The following is a list of the best classes of packing-house grease obtainable in commerce :—

White Grease A.—This is made from dead hogs, and in general from lard unfit for edible purposes. (See Vol. II. Chap. XIV. p. 702).

White Grease B.—This is an inferior grade made from the same source.

Yellow Grease consists of the fat from waste portions of all animals, chiefly hogs. This grease is generally mixed in the large establishments of the United States with " kitchen grease," *i.e.* all kinds of waste fats collected from private houses, hotels, restaurants, etc.

Brown Grease represents the lowest grade of packing-house grease, and is made from all kinds of offal.

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[1] For the separation of fat from " soup," cp. German patents 211,574 and 220,843 (Actien-Maschinenbau Anst. vorm. Venuleth and Ellenberger and Schmidt); also Meyer, German patent 212,643.

[2] Dörner, German patent 218,487.

[3] Lehbauer, Mear, Hollingshead and Moody, English patent 21,630, 1908.

(*b*) Bone Grease

In large establishments all refuse bones which have not been worked up for "neats' foot oil" (Vol. II. Chap. XIV. p. 492) and "bone fat" (see Vol. II. Chap. XIV. p. 756) are kept separate as "bone tankage," and yield "bone grease." "Bone grease" is inferior in quality to the "bone fats" (Vol. II. Chap. XIV. p. 756) obtained by the "boiling-out process." (Two analyses of such greases are given in the table below.) A variety of this kind of grease is "pig's foot grease" (see Vol. II. Chap. XIV. p. 702). The benzine extracted bone greases have been described at length in Vol. II. p. 757).

(*c*) Skin Grease

French—*Graisse de peaux.* German—*Hautfett.*

Skin grease is obtained as a by-product in cleaning (scraping) the skins of animals, preparatory to the tanning, etc., process. In this manner the best kinds of skin grease—"white skin grease" and "light skin grease"—are obtained.

As it is impossible to remove the whole amount of fat by this mechanical process, especially from "pickled" sheepskins, expression of the skins in hydraulic presses (see Vol. II. Chap. XIII.) at a slightly elevated temperature is resorted to in modern establishments.

An apparatus for extracting sheep's skins with carbon tetrachloride has been patented by *Charles Dent and Abel* for the Société de lainage Verviétois Peltzer et Cie.[1] The greases so obtained are somewhat dark in colour; they are sold as "brown skin grease" or "dark skin grease." The skin greases described here must not be confounded with the grease obtained from tanned or tawed skins or clippings (see below, p. 442).

(*d*) Grease from Carcase-rendering Establishments—Carcase Fat

French—*Graisse de carcasse*; *graisse d'équarrissage*; *graisse de crinière.* German—*Abdeckereifett, Kadaverfett.*

Since it has been demonstrated that the primitive methods of disposal of dead animals (by interring, or by cremating in the open, etc.) formed one of the most fruitful sources of spreading contagious diseases, sanitary authorities in all civilised countries prescribe stringent rules for the destruction, or for the odourless rendering and drying of this objectionable material. The practice of the large packing-houses has served as the prototype, and in most of the large towns special establishments have been erected in which carcases are rendered innocuous, whilst being worked up at the same time for commercial products. In some of the modern installations designed on the Continent, there seems to prevail a tendency to lay more stress on the profits which may be derived from the recovery of the by-products than on the primary demand that the material be rendered harmless at any cost. Thus stress is not only laid on the obtainment of the most valuable product—the greases—but attempts are also made to work the residues into food for domestic animals, instead of disposing of them as “fertiliser.” A detailed discussion of these installations falls outside the scope of this work, and for a description of some plants introduced on the Continent the reader must be referred to the works quoted in the footnote.[1] The principle employed in the different installations is the same as that used in the large packing-houses of the United States. Dead animals, etc., are thrown into large digesters, in which they are treated with live steam under pressure (in some cases with close steam, the moisture contained in the carcase being relied upon to supply the necessary water) when the fat rises to the top, whilst the solid portions fall to the bottom, and an intermediate aqueous layer, holding gluey substances in solution or in an emulsion, is obtained. The fat is recovered in the same manner as described under “tankage” fats. As sanitary authorities do not (or should not) permit the aqueous solution to be run into sewers, it is evaporated in vacuum evaporators, and worked up into low-class glue, etc.

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[1] English patent 2360, 1900

The fat so obtained is a mixture of tallow, lard, and also of horse fat (cp. Vol. II. p. 686).

(*e*) “Animal Greases”—“Animal Oils”

French—*Graisses animales*; *huiles animales.*

Under this indefinite name a great variety of solid or semi-liquid greases are sold, which differ considerably in quality. The best kinds of “animal greases” would approach those described under (*a*), just as the best kinds of “animal oils” would be represented by low grades of neats’ foot oil, horses’ foot oil, horse oil, tallow oil, lard oil. Under the term “animal grease,” or “animal oil,” must be understood, however, waste fats and oils from refuse tallow, scrap fat, skin grease, and all kinds of animal refuse fats and oils (horse fat, horse oil). As a rule, they are of a very dark colour, or almost black. They mostly possess a very offensive smell, and contain any proportion of free fatty acids from 10 to 50 per cent, and even more. The proportion of unsaponifiable matter in this class of greases is, as a rule, very high; not infrequently it is increased by the fraudulent admixture of low-class (dark) mineral oils, “recovered grease,” “black grease,” etc.

In the following table I collate some analyses of commercial greases:—

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[1] Heepke, *Die Kadaver-Vernichtungsanlagen*, Halle a/S, 1905; Haefcke, *Handbuch des Abdeckereiwesens*, Berlin, 1906; P. Naumann, *Gesundheits-Ingenieur*, 1908, 225. More recently patented apparatus, not described in these works, are those by the Actien-Maschinenbau-Anstalt vorm. Venuleth und Ellenberger, French patent 394,076; Lehbauer, S. Mear, E. W. Hollingshead and H. E. Moody, English patent 21,630, 1908; Frabot, *Ann. chim. analyt.*, 1919, i. 55-65.

Analyses of Greases (Lewkowitsch)

	Ash.	Free Fatty Acids.	Neutral Fat.	Unsaponifiable.	Iodine Value.	Titer Test.	Moisture.
	Per cent.	Per cent.	Per cent.	Per cent.		° C.	Per cent.
Bone grease I.	0·63	62·1	32·4	1·78	...	...	1·79
" II.	4·48	10·4	42·1	20·94	...	...	...
White skin grease	...	3·6	96·0	...	...	...	...
Light skin grease	0·077	12·3	86·0	...	...	...	...
Brown skin grease	0·03	13·9	77·2	9·1	50·5	37·9	0·88
" "	...	46·2	27·1	22·1	...	...	...
Dark skin grease	1·78	22·7	60·7	...	...	...	...
" "	...	24·0	64·0	...	...	...	...
Green skin grease	...	40·1	33·3	21·9	...	...	...
"Animal grease"	0·96	31·4	65·7	2·8	46·4	39·6	5·90
"Animal oil"	...	35·4	...	45·4	...	...	...

(*f*) “Fish Stearine”—“Whale Grease”

French—“*Stéarine*” *de poissons*; *suif de balaine.*

The manufacture of “stearines,” as obtained from individual species of animals, has been described under the heading of “Fish Oil,” “Seal Oil,” “Whale Oil.” The practice of large rendering establishments for fish oil, etc., simulates that of the packing-houses. The “fish-stearine” of commerce is of varying composition, and represents either the solid glycerides from fish oils, cod liver oil, seal oil, whale oil, or a mixture of all these “stearines.” (With regard to “Whale Bone Oil,” see Vol. II. p. 469.)

The following table, due to *Hajek*, gives six analyses of “fish stearines.”

Analyses of Fish Stearines

Fish Stearine.	Fat.					Fatty Acids.	
	Impurities.[1]	Melting Point.	Iodine Value.	Acid Value.	Fatty Acids.	Solidifying Point.	Melting Point.
No.	Per cent.	° C.	Per cent.		Per cent.	° C.	° C.
1	4·0	43·5	42·3	16·9	90·2	...	44·5
2	5·6	40·0	44·0	20·9	91·0	...	38·0
3	5·7	46·5	41·0	30·0	90·0	43·0	45·0
4	5·2	...	...	20·0	91·0	42·5	44·75
5	6·0	44·5	...	40·0	95·5	41·75	43·50
6	15·0	46·5	...	...	80·8	...	45·0

The rank, fishy odour which adheres persistently to these “stearines” renders them almost useless for soap-making, and they are therefore chiefly worked up into dégras-substitutes, stuffing-greases, etc. This holds good also of the distilled fatty acids from fish oils, which were brought into commerce on the Continent, under the fancy name “Olid” fatty acids. Modern modes of rendering whales, etc., make the first-class stearine an important and valuable article of commerce.

G. Weiss[2] patents a method for deodorising fish oils in which the oil or its fatty acids are heated to 200° C. with alkalis or alkaline earths.

The best classes of greases considered in this chapter are used as substitutes for tallow, lard, etc., in the soap and candle industries. Lower kinds, provided their colour be not too objectionable, and the proportion of unsaponifiable matter be not too high, may be used for low-class soaps. Still lower products are worked up into lubricating greases, dégras-substitutes (see below), and stuffing-greases. The lowest kinds, such as “animal grease” and “animal oil,” are treated with sulphuric acid, and subsequently worked up into “oleine” and “stearine” by distillation, much in the same manner as “black grease” is treated.

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[1] The impurities include all non-fatty (especially gelatin-like) substances.

[2] German patent 294,136, 1913.

As an example may be given the working up of " fish stearine." Although this waste fat is at present of no practical importance to the candle-maker, the results published by *Hajek*[1] are recorded here, as they may deserve attention in case fats again reach the high prices of the last few years.

A somewhat large quantity of washed and dried " fish stearine " containing 7 per cent of " impurities " was autoclaved with 2·5 per cent of lime at a pressure of eight atmospheres during seven hours, and is stated by *Hajek* to have yielded 94 per cent of crude fatty acids, containing 3 per cent of unsaponifiable matter. The yield of glycerin of 28° Bé. is stated to have been 7·3 per cent of the autoclaved mass. The fatty acids were then distilled ; nine samples taken at intervals of two hours showed the following characteristics :—

Sample.	Colour.	Appearance.	Solidifying Point.	Melting Point.
No.			°C.	°C.
1	Green	Forming scales	46	48·75
2	,,	,,	47·1	49·2
3	White	Amorphous, containing some crystals	47·5	49·5
4	,,		47·75	50·0
5	,,		48·50	50·25
6	Greyish white		48·75	50·75
7	Grey		47·50	49·50
8	,,		42·50	44·50
9	,,	Viscous	...	36·00

The total yield obtained on distillation is given as follows :—

	Per cent.
Fatty Acids	95·77
Stearine Pitch (Goudron)	3·50
Loss (by difference)	0·73
	100·00

Laboratory experiments carried out with a view to increasing the yield of candle material by acidifying the fatty acids before distillation (cp. " Mixed Process," Chap. XV.) did not lead to satisfactory results.[2] A summary of the large scale experiment is given in the following table :—

	Per cent.
" Stearine " (candle material) . . .	53·10
Oleine	36·90
Stearine Pitch (Goudron)	3·29
Glycerin, 28° Bé.	7·00
	100·29

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[1] *Seifensieder Zeit.*, 1903, 580.

[2] Cp., however, C. K. Keutgen, *Seifensieder Zeit.*, 1915, 42, 552-553, 573-574, 594-595, 617-618.

2. Sod Oil—Dégras[1]

French—*Dégras, Moëllon.* German—*Gerberfett* (*Lederfett*[2]), *Weissbrühefett, Dégras*

Sod oil or dégras[3] is the waste fat obtained in the chamoising process, and is used for currying purposes, *i.e.* dressing bark-tanned or chrome-tanned leather.

The skins which are to be converted into chamois leather are first "limed," whereby they swell and the roots of the hair are loosened; the hair is then removed by the aid of a blunt dressing knife, and the unhaired hides are next split in a special machine into "grain" and flesh and then "drenched," *i.e.* placed in a "sour bath," made of bran and water, in which they are neutralised in consequence of an acid fermentation (due to *Bacterium furfuris*) setting in. The skins are stretched and well rubbed with whale or cod liver oil[4]—in the United States with menhaden oil[5]—and worked in a fulling machine, "stocks," so as to become thoroughly saturated with oil. Then the skins are taken out and exposed to the air. The same process of rubbing with oil and stamping in the stocks is repeated until enough oil has been absorbed, and the skins appear quite dry. In consequence of the exposure to the air, a portion of the oil has been changed, and has entered (as the "practical man" terms it) into "combination" with the fibre, another portion being only mechanically enclosed within the pores of the skin. The "combined oil" is that portion of altered fatty matter which cannot be extracted by carbon bisulphide.[6] In order to render the "combination" of the oil with the fibre more rapid, a fermentation attended with elevation of temperature is brought about by heaping the skins together in a warm room, and covering them carefully with canvas so as to keep the generated heat in the heap. Overheating, however, must be prevented by occasionally turning over the pile so as to cool the skins. The "oxidation of the oil" is considered to be complete when the skins have acquired the yellow colour of chamois leather.

From the foregoing description, which represents the views held by "practical men," it will be evident that the actual changes which occur in the chamoising process are but very incompletely understood.

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[1] Jean, *Moniteur Scientifique*, 15, 1889. Eitner, *Der Gerber*, 1890, 85. Simand, *Der Gerber*, 1890, 243, 254, 266, 279. Jahoda, *Zeits. f. angew. Chem.*, 1891, 325. Fahrion, *Journ. Soc. Chem. Ind.*, 1891, 557, 1013; 1893, 937. Ruhsam, *Journ. Soc. Chem. Ind.*, 1892, 639. Weiss, *Journ. Soc. Chem. Ind.*, 1893, 937. Eitner, *Der Gerber*, 1893, 257. Schmitz-Dumont, *Dingl. Polyt. Journ.*, 1895, 296, Nos. 9-11; *Journ. Soc. Chem. Ind.*, 1895, 815, 829. Tortelli, *Annali del Lab. Chim. delle Gabelle*, 1897, 184.

[2] This term is a very indefinite one, as it also embraces "stuffing-grease" and leather-greases obtained from tanned skins and from leather clippings.

[3] It should be noted that in the United States "dégras" denotes the recovered grease from wool-scouring works.

[4] With regard to a method of examining cod liver oils for tanning purposes, cp. Trotman and Peters, *Journ. Soc. Chem. Ind.*, 1902, 694.

[5] "Alligator oil" is also stated to be used for this purpose. Hitherto this oil, said to be sold under the name *Jacare oil*, has not been obtainable in Europe (*American Soap Journ.*, 1906 (16), 213.

[6] Cp. v. Schroeder and Paessler, *Journ. Soc. Chem. Ind.*, 1895, 759.

It seems most likely that in the first instance the glycerides are hydrolysed to glycerol and free fatty acids.[1] The glycerin would remain unchanged, and is washed away later on, whereas the unsaturated fatty acids are readily oxidised under the favourable conditions present (access of air at an elevated temperature and presence of putrescible organic matter). The nature of the oxidised fatty acids is completely unknown as yet, and it need, therefore, only be pointed out that *Fahrion*[2] conjectures that the unsaturated fatty acids are converted into "peroxides" (cp. also below "dégras-former"). A certain amount of confirmation of this view may be found in the fact that unsaturated acids are somewhat easily converted by ozone into ozonised fatty acids.

Most of the oil originally applied is found to be left in the "uncombined" state, and is removed by one of the two following methods:—

English and German Method.—If no more oil can be recovered by pressing or wringing, the excess is removed from the skins by washing with alkaline lyes. The emulsion thus obtained is similar to a wool grease emulsion; like the latter it is acidified with sulphuric acid and the fatty matter separating as an upper layer is skimmed off. This fatty substance forms the *sod oil* of commerce.

Sod oil, in contradistinction to dégras, contains a considerable amount of water, soap, and impurities, such as hide fragments, etc. The sod oil is frequently dehydrated[3] by heating in a jacketed pan, when the water is either evaporated off or settles out at the bottom of the pan. Such oil is, however, as *Procter*[3] states, no suitable substitute for the genuine dégras prepared by the French method.

According to *Procter*,[3] many English manufacturers have adopted the French process, so that their product does not differ from French moellon. It is a mistake to "evaporate" such sod oil, as the value greatly depends on the state of emulsion in which it is kept by the water.

French Method.—The skins are "stocked," aired, and fermented for a shorter period than by the English or German process, so that a large proportion of the oil can be obtained from the skins by steeping them in warm water and wringing or pressing in hydraulic presses. The oil thus obtained is called "première torse" *moellon.* The oil still retained by the skins is recovered by washing with alkali, as is done in the English and German methods, and this is usually added to the moellon.

Whereas genuine *moellon* consists only of expressed oil, a second quality termed "secunda dégras," or shortly "dégras," is prepared by mixing genuine moellon with blubber oils, or neats' foot oil, or solid fats (such as tallow, palm kernel oil). This product is still included amongst better qualities of dégras. In fact, according to *Procter*, pure moellon is never sold as such, but is always mixed with tallow and untreated oils; these admixtures cannot, therefore, be regarded as adulterants.

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[1] Indeed André Piedaller (*Compt. rend.*, 1909, 510) found the fungus *Monascus purpureus* on hides undergoing chamoising, and ascribed the hydrolysing action to an oxydase which is secreted by the fungus.

[2] *Chem. Zeit.*, 1903, 670; *Zeits. f. angew. Chem.*, 1909, 2083; 2135.

[3] *Leather Industries Laboratory Book*, 1898, 204.

Numerous " substitutes " of dégras, or artificial dégras (" corroïne "), occur in commerce, consisting of highly adulterated dégras, or of more or less judiciously prepared mixtures of cod, whale, menhaden, sardine, Japan fish oils, blown blubber oils,[1] fish stearines, tallow,[2] rosin, oleic acid, " recovered grease " (p. 448), mineral oil, etc.

In order to satisfy the great demand for dégras, skins are frequently worked up simply for its production, being oiled and pressed until not a rag is left. Dégras thus prepared must still be considered genuine.

Both sod oil and dégras contain considerable quantities of water, which is held in suspension in the form of an emulsion. According to *Jean*, the emulsifying agent is a " resinous substance " (*dégragène*) formed in the course of the oxidation of the oil.

This " resinous substance " is an acid ; it has a brown colour, melts at 65°-67° C., dissolves in alkali, but is not precipitated by common salt from its alkaline solutions ; it is insoluble in water, soluble in alcohol and ether, but *insoluble in petroleum ether.*

Simand described the same substance under the name " dégras-former." This " resinous substance," or " dégras-former," is an oxidation product (cp. Vol. I.), and most likely belongs to the class of oxidised acids. In *Fahrion's*[3] opinion the " dégras-former " is a mixture of oxidised acids (peroxides ; see above) and their anhydrides.

It is desirable that the use of such unscientific names as " dégras-former," " resinous substance," be discontinued.

Most sod oils and dégras contain *unsaponifiable substances*, introduced to some extent with the unsaponifiable matter originally contained in the marine animal oils used in their preparation.

The *specific gravity* of dehydrated dégras is of course higher than that of the oils from which it is prepared ; it varies from 0·945 to 0·955. The specific gravity of dégras containing water approaches 1·00. If the dehydrated dégras has a lower specific gravity than 0·920, admixture of mineral oil may be suspected.[4]

An examination of several marine animal oils, according to *Livache's* method (Vol. I. Chap. VII.), proved, in satisfactory agreement with practical experience, that the oils that are best suited for the production of dégras absorb the highest amount of oxygen. The proportions of oxygen absorbed by oiled skins have been given, Vol. I. Chap. VII. It will be gathered that whale oil is most suitable for this purpose, whereas sperm oil is almost useless.

The following table, due to *Eitner*,[5] is instructive, as showing the difference between natural oils and their corresponding sod oils :—

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[1] Schill and Seilacher have patented two methods for preparing artificial dégras, viz. by blowing blubber oils with air, and by treating with hydrogen peroxide.

[2] Of course, only very low qualities of tallow from waste fats will be used for this purpose.

[3] *Journ. Soc. Chem. Ind.*, 1891, 558.

[4] With regard to the determination of the specific gravity and a criticism of *Simand's* procedure, cp. Gawalowski, *Wiener allg. Gerber-Zeit.*, 1903, No. 2.

[5] *Der Gerber*, 1893, 257.

Name of Oil.	Specific Gravity.		Refractive Index.		Fatty Acids Insoluble in Petroleum Ether.		Acid Value.		Saponification Value.		Acetyl Value.[1]		Iodine Value.	
	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.
					Per cent.									
Shark liver oil	0·9158	0·9212	1·4735	1·4752	0·91	1·70	7·0	8·4	157·2	143·2	45·0	45	90	82·4
Seal oil	0·9258	0·9465	1·4760	1·4790	2·70	14·41	6·1	26·1	193·8	190·5	25·6	47·8	96·5	68·4
Mixed fatty acids from seal oil	0·9354	0·9473	...	...	3·0	15·51	...	...	...	...	...	...	...	...
Cod liver oil	0·9274	0·9836	1·4755	1·4780	0·87	19·40	13·6	28·3	187·9	183·4	19·4	28·3	148	100·5
Mixed fatty acids from cod liver oil	0·9375	0·9612	...	...	1·21	18·44	...	...	...	...	...	...	...	...
Whale oil	0·9270	0·9423	1·4755	1·4758	3·44	6·19	10·6	10·6	190·4	181·5	14·0	22·0	85	71

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[1] These numbers stand in need of confirmation, having been determined by Benedikt and Ulzer's method.

EXAMINATION OF SOD OIL AND DÉGRAS

1. **Determination of Water.**—10 grms. of the sample are mixed with a sufficient quantity of sand to give a solid and almost dry mass. This is dried at 120° C. to approximately constant weight. *Fahrion* proposed the following *modus operandi*, which has been adopted by the International Association of Leather Trade Chemists:—Heat 10 grms. slowly in a platinum crucible over a small flame until all the water has been driven off; the end of the operation is recognised by the appearance of a slight evolution of vapours. The method given by *Hopkins, Coburn, and Spiller*[1] has been abandoned as incorrect. A comparative study of the methods proposed for the determination of water in sod oil and moellon has been made by *F. W. Alden.*[2]

French dégras contains, as a rule, from 15 to 25 per cent of water, sod oil from 20 to 40 per cent (cp. tables below).

2. **Ash.**—This is determined in the usual manner.[3] If the ash has an alkaline reaction, pointing to the presence of soap in the dégras, the amount of the latter may be approximately determined by boiling the ash with water, filtering and titrating the filtrate with standardised acid. The amount of carbonate thus found may be calculated to soap.

French dégras contains but a few hundredths per cent of ash, sod oil as much as 3 per cent. The ash should be examined for iron, as iron in dégras is apt to stain leather.[4]

3. **Mineral Acids.**—A preliminary test is made with litmus paper. If the dégras is found acid, the sample is boiled out with water, and the aqueous layer is titrated with standard alkali, using methyl-orange as an indicator.

Schmitz-Dumont drew attention to the possible presence of soluble fatty acids. He advises to exhaust the aqueous solution with ether. It may be more expeditious to titrate the mineral acids as described, then to add phenolphthalein, and to titrate again until the solution becomes pink.

4. **Total Impurities.**—10 grms. are digested with petroleum ether boiling below 75° C., and the solution is filtered off. The residue on the filter is then washed with ordinary ether to remove any free oxidised acids, and the residue is weighed. The difference between the weight of the residue and the weight of ash gives the amount of organic impurities. These latter consist of soap and of hide fragments. The soap may be removed by washing the residue with water, and subsequently with alcohol. The residue left on the filter is weighed, incinerated, and

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[1] Third edition of this work, p. 1124.

[2] *Journ. Amer. Leather Chem. Assoc.*, 1907, 12; 1908, 335 (L. E. Levi and E. V. Manuel); cp. also Fahrion, *Collegium*, 1908, 21.

[3] According to *Villon*, a syrupy solution of magnesium chloride is extensively used for mixing with dégras. 20 per cent of this concentrated solution may be added without being detected by the appearance of the dégras or by an abnormal proportion of water.

[4] *Simand* states that as little as 0·05 per cent of ferric oxide has an injurious action. Addition of 500 c.c. of a 1 per cent oxalic acid solution to 100 kg. of dégras is said to remedy this defect.

weighed again. The difference between the two weights gives the approximate weight of hide fragments. The petroleum ether extract gives the amount of fatty matter *free from oxidised acids*; the ether extract contains chiefly the oxidised acids, together with small quantities of dissolved soap. The amount of the latter may be determined by incinerating and calculating the amount of sodium carbonate found in the ash to soap, the fatty acids of which may be assumed to have the mean molecular weight 300.

5. **Unsaponifiable Matter.**—This is isolated by saponifying the fatty matter, and extracting either the soap solution with ether, or the dried-down soap with petroleum ether. The unsaponifiable matter may be examined according to the methods described in Vol. I. Chap. IX. According to *Meunier and Vaney*,[1] the amount of unsaponifiable matter varies from 1 to 6 per cent, calculated on the anhydrous dégras. If it exceed the highest figure, adulteration with hydrocarbons, or wool grease (cp. p. 448), or distilled grease must be suspected. The detection of cholesterol is not sufficient proof of the presence of *wool grease* or *distilled grease*, as low-class fish and liver oils contain notable proportions of this alcohol; but the appearance of a green fluorescence would point to the presence of isocholesterol, and inferentially to that of wool grease or of distilled grease. Since raw wool grease is not completely saponified by means of half-normal alcoholic potash, part of its waxes passes into the unsaponifiable portion. If, on saponifying the latter under pressure, or with sodium alcoholate, a definite saponification value is obtained, the presence of wool wax may be suspected. From the saponification value thus determined the quantity of wool wax may be approximately calculated. Confirmation is obtained by acetylating the unsaponifiable matter, and examining it according to the methods described in Vol. I. Chap. IX. Small proportions of vaseline should not be looked upon as adulterants according to *Paessler*, as this is mostly added in order to give the dégras the proper consistence.[2]

6. **Oxidised Acids.**—These are recovered from the ether extract obtained as described under 4. It is, however, preferable to determine their amount in a fresh quantity of the sample by *Fahrion's* method described in Vol. I. Chap. VIII.

According to *Simand*, a sample may be considered pure if it yield at least 12 per cent of oxidised acids, calculated to a dégras containing 20 per cent of water. Good samples contain higher proportions of oxidised acids. According to *Meunier and Vaney*,[3] however, even 12 per cent is too high, for most French moellons of excellent quality contain much less, mostly from 2 to 10 per cent.

7. **Free Fatty Acids.**—These are determined in the usual manner (Vol. I. Chap VI.). The free fatty acids are usually calculated to oleic acid. The fatty matter obtained from dégras contains, as a rule, 15 to 20 per cent of free fatty acids. In the commercial valuation of dégras

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[1] *La Tannerie*, p. 508.

[2] *Berichte d. deutsch. Versuchsanst. f. Lederindustrie*, 1908.

[3] *La Tannerie*, p. 501.

and sod oil the proportion of free fatty acids plays, however, no important part.

Jean gives the following analyses of seven samples of dégras :—

		1	2	3	4	5	6	7
Water . .	per cent	18·90	14·84	12·93	28·90	19·20	5·39	8·90
Ash . . .	,,	0·25	0·13	0·55	0·70	0·07	0·25	1·21
Hide fragments .	,,	0·30	0·30	0·09	0·58	0·27	...	1·59
Oils . . .	,,	69·71	74·65	80·00	66·93	75·66	84·87	72·15
Unsaponifiable .	,,	6·84	6·05	...	...	...	...	...
Oxidised acids .	,,	4·00	4·05	5·81	3·52	4·80	9·46	16·15

The following table reproduces *Simand's* analyses of some specimens of dégras and of sod oil :—

	Oxidised Acids.	Melting Point of Fatty Acids.	Soap.	Original Dégras.	
				Hide Fragments.	Water.
	Per cent.	° C.	Per cent.	Per cent.	Per cent.
French dégras, anhydrous No. 1	19·14	18·0-28·5	0·73	0·07	16·5
,, ,, ,, 2	18·43	28·5-29·0	0·49	0·12	20·5
,, ,, ,, 3	18·10	31·0-31·5	0·68	0·18	12·0
Sod oil ,, ,, 1	20·57	33·5-34·0	3·95	5·7	35·0
,, ,, ,, 2	18·63	27·0-27·5	3·45	5·9	28·0
,, ,, ,, 3	17·84	28·0-28·5	3·00	4·5	30·5

The quantitative reactions, such as the determination of the saponification and iodine values, have been used by several chemists in the examination of dégras. It should, however, be borne in mind that in this case they afford but little discriminative value. A large quantity of mineral oils is more readily detected by the determination and examination of the unsaponifiable matter than by the saponification value.

An exhaustive examination of a number of dégras by the usual quantitative methods was made by *Rusham*.[1] His results are given in the following table :—

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[1] *Journ. Soc. Chem. Ind.*, 1892, 639.

No. of Sample.	Water.	Iodine Value.				Acid Value.		Saponification Value.		Mgrms of KO per gra corre- spondi to Lactone
		Original Dégras.	Anhydrous Dégras.	Insoluble Fatty Acids.	Acetylated Fatty Acids.	Original Dégras.	Anhydrous Dégras.	Original Dégras.	Anhydrous Dégras	
	Per cent.									
1	19·1	60·4	74·7	70·5	73·1	30·5	37·7	...	...	38·8
2	12·9	55·9	64·2	58·6	52·7	63·3	72·7	96·2	110·4	28·7
3	12·4	67·8	77·4	75·4	90·4	35·2	40·2	97·0	110·7	43·4
4	15·9	65·9	78·4	70·2	66·6	42·1	50·1	113·4	134·8	30·8
5	16·4	65·0	77·8	78·5	76·2	44·1	52·7	114·9	137·4	22·4
6	11·5	67·8	76·6	76·5	75·7	57·4	64·9	96·3	108·8	53·8
7	13·9	83·3	96·7	95·9	88·9	...	...	...	...	33·1
8	17·3	69·2	83·7	93·4	102·7	23·9	28·9	83·4	100·8	100·4
9	16·6	67·5	80·9	...	...	43·4	52·0	117·8	141·2	...
10	5·3	70·5	74·4	79·3	73·0	51·2	54·1	118·6	125·2	30·7
11	...	127·7	127·7	142·3	127·4	..	...	...	163·8	31·4
12	...	...	126·7	106·0	101·9	...	...	...	186·0	53·9
Mean of 1-10	...	...	78·5	77·6	77·7	...	50·4	...	121·2	42·4

The samples 1-9 represent French artificial dégras. No. 10 is a so-called "emulsion fat," No 11 a moellon prepared by *Ruhsam* from the whale oil described under No. 12. The acetyl values given in the original paper have been omitted here for the reasons stated in Vol. I. Chap. VI.

Schmitz-Dumont's results, obtained in the examination of a number of dégras and commercial products yielding high proportions of unsaponifiable matter, are contained in the following table :—

[TABLE

No.			Water.	Ash.	Insoluble in Petroleum Ether.	Fatty Matter.	Un-saponifiable Matter.	Oxidised Acids.	Anhydrous Fat.		
									Acid Value.	Saponific. Value.	Iodine Value.
			Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.			
1		Dégras	13·31	0·32	0·31	86·1	3·1	11·03	108·0	185·8	69
2		,,	10·05	0·18	0·24	89·5	3·4	14·13	119·0	188·0	52·8
3		,,	10·24	0·28	0·28	89·2	1·0	1·49	104·0	181·8	70·7
4		,,	8·49	0·06	0·31	91·1	0·91	9·25	34·5	208·5	106·0
5		,,	17·33	0·27	0·14	82·3	2·51	0·95	29·2	206·0	122·0
6		,,	10·59	0·20	0·10	89·1	3·1	10·93	112·0	181·2	63·9
7		,,	1·53	0·70	0·04	97·7	1·85	16·17	112·0	170	62·5
8		Moëllon, pure	18·45	0·07	0·09	81·4	2·04	11·65	25·7	215·5	89·1
9		,,	19·88	0·03	0·46	79·63	0·45	1·46	47·4	214·0	115·0
10		Moëllon-dégras	11·65	0·63	0·98	86·74	3·27	2·01	17·4	196·7	126·0
11		Oxidised blubber oil	10·43	0·50	0·21	88·86	1·44	1·61	17·0	192·3	129·0
12		Oxidised emulsion fat	7·45	0·41	0·08	92·1	2·72	9·74	17·0	196·3	107·8
13	Of French origin	Dégras	13·88	0·14	0 22	86·8	40·6	4·06	35·0	99·8	52·9
14		,,	14·16	0·58	0·97	84·3	18·9	3·73	32·4	137·4	80·6
15		,,	25·46	0 07	1·25	73·22	14·29	5·99	33·0	206·4	101·8
16		,,	18·79	0·46	0·31	80·44	23·61	5·33	31·0	135·4	72·3
17		Dégras-moëllon	15·79	0·05	0·22	83·94	28·1	1·84	40·5	113·2	72·1
18		Dégras	7·59	0·26	0·38	91·8	33·12	8·39	39·7	93·0	49·9
19		"Mutton dégras"	16·49	0·31	0·74	82·5	8·5	5·51	39·4	194·0	104·5
20		Dégras moëllon	14·29	0·29	0·38	85·04	14·1	4·96	38·4	180·0	102·0
21		Dégras	20·37	0·08	0·45	79·1	40·3	2·95	24·0	86·0	49·5
22		,,	30·29	0·25	0·22	69·24	2·23	6·55	54·6	201·0	90·0
23		Fat from sod oil	..	..	..	100·0	0·71	16·84	71·3	234·0	61·0

Similar analyses, published by *Tortelli*, are reproduced in the following table :—

No.		Specific Gravity at 18° C.	Water.	Ash.	Insoluble in Petroleum Ether.	SO_3.	Unsaponifiable Matter.	Oxidised Acids		Acid Value of		Saponification Value of		Iodine Value of	
			Per cent.	Per cent.	Per cent	Per cent.	Per cent.	in Original Substance.	in Anhydrous Substance.	Original Substance.	Anhydrous Substance (calculated).	Original Substance.	Anhydrous Substance (calculated).	Original Substance.[1]	Anhydrous Substance (calculated).
1	Natural dégras from chamoising .	1·0025	31·13	1·83	5·07	0·47	2·36	18·03	26·38	35·75	51·75	155·0	221·0	35·7	52·3
2	" " " .	0·9993	39·60	1·79	5·18	0·20	1·26	14·09	23·44	25·08	41·72	144·0	239·0	34·0	56·4
3	Fish oil, used in dégras manufacture	0·9172	0·20	0·03	...	0·0	1·30	3·79	3·80	9·39	...	192·3	192·3	139·7	139·7
4	Commercial "dégras," German .	0·9435	17·74	0·11	0·15	0·0	1·16	9·66	11·77	16·64	20·02	172·0	209·0	69·0	83·8
5	" " French .	0·9495	18·13	0·32	trace	0·0	19·61	2·03	2·48	22·49	27·46	131·2	160·0	64·4	78·9
6	" " French .	0·9445	17·35	0·49	trace	0·03	2·25	6·65	8·04	11·72	14·18	164·0	198·0	95·6	115·6
7	" " French .	0·9466	20·78	0·38	trace	0·04	1·88	9·44	11·92	11·55	19·62	160·0	193·0	53·8	65·3
8	" " German .	0·9493	22·89	0·60	0·23	0·02	8·75	9·11	11·81	11·83	15·35	126·0	163·4	44·7	58·0
9	" " German .	0·9493	21·33	0·55	0·30	0·06	15·77	4·30	5·47	11·49	14·61	105·0	129·0	39·6	50·4
10	" " French .	0·9498	21·40	0·10	0·12	0·02	30·56	5·40	6·87	19·29	24·54	95·0	120·9	45·4	57·7
11	" " Belgian .	0·9506	22·70	0·08	0·32	0·04	22·26	6·18	7·99	18·77	24·28	92·5	119·2	46·1	59·6
12	" " Belgian .	0·9516	10·89	0·31	0·86	0·02	17·59	4·90	5·50	12·63	14·27	136·0	152·6	50·2	50·7

[1] The iodine value was determined in the substance containing water.

Hopkins, Coburn, and Spiller[1] examined twelve American sod oils. The maxima and minima are given in the following table. The numbers are calculated in terms of anhydrous sod oil :—

	Water.	Ash.	Mineral Acid in terms of KOH.	Oil, etc., soluble in Petroleum Spirit.	Soap, etc., soluble in Alcohol.	Hide Fragments.	Unsaponifiable Matter.	Oxidised Acids.	Free Fatty Acids.
	Per cent.	Per cent.		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Minimum	1·01	0·05	1·13	56·62	0·68	0·15	0·37	1·09	32·65
Maximum	40·61	1·045	91·51	96·60	8·81	2·99	42·62	26·44	34·26

Artificial Dégras

It has been pointed out already that pure moellon is, as a rule, mixed with tallow and untreated oils ; hence these admixtures cannot be regarded as adulterants. Frequently even vegetable oils are admixed to dégras. A large number of artificial dégras are now made by blowing fish, liver, and blubber oils[2] with air, in the manner in which "blown oils" are prepared, or by treating with ozone, in the hope of imitating the natural process of oxidation which the oils appear to undergo whilst skins are being converted into chamois leather. Thus *Baron*[3] prepared an artificial dégras by blowing neutral wool fat and cod liver oil or whale oil, finally treating the mixture with hydrogen peroxide and water. This product forms an emulsion with water. These blown oils are frequently adulterated with mineral oil.

A number of artificial dégras are now offered under fancy names, such as "*Corroïne*" (a mixture of vaseline and wool fat, emulsified with water[4]), "*Aërisine*" (blown rosin oils), etc.[5] It need hardly be pointed out that such products are harmful preparations.

3. STUFFING-GREASES

French—*Enduit pour peaux.* German—*Ledereinfettungsmittel,*
Lederschmieren

Stuffing-greases consist of a mixture of dégras with horse fat, skin grease, bone fat, and tallow, or of a mixture of tallow and fish stearine,[6] and similar waste fats (see 1. "Greases," p. 422). In some cases a certain proportion of *soft* soap is admixed. Frequently the ammonia soaps of rape oil are used. Some stuffing-greases are nothing else but distilled grease stearine (p. 459) or even " recovered grease " (p. 448); others again contain a considerable proportion of hydrocarbons of high specific gravity, tar oils, mineral waxes, rosin,[1] and even of lime. The last-mentioned stuffing-greases must be looked upon as adulterated articles which are likely to act detrimentally on the leather.

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[1] *Journ. Amer. Chem. Soc.*, 1899, 291.

[2] Cp. Schill and Seilacher, footnote 1, p. 431.

[3] *Rev. Chim. Ind.*, 1897, 225.

[4] *Journ. Soc. Chem. Ind.*, 1895, 815.

[5] Cp. French patent 356,936 (L. Vultée) ; French patent 357,525 ; German patent 166,752 (Schowalter).

[6] "Dubbin," a mixture of tallow and cod oil, serves the same purpose.

Stuffing-grease for tanned leather (such as is used for kid gloves) contains egg oil (see Vol. II. Chap. XIV. p. 491).

Stuffing-greases are employed to give tanned leather the suppleness and pliability which is demanded of the finished article, and to render it at the same time water-proof. In order to render leather impervious to water the application of a mixture of beeswax, paraffin wax, rubber solution and mineral oil has been patented by *Fölsch*.[2] The oils and fats used for this purpose do not act merely as a lubricant, for a lubricating oil (or grease) would not fulfil the desired object, but would rather tend to pass through the leather and reappear at the under side as a grease stain. (This happens if, *e.g.* castor oil or ordinary fish oil is used in place of a proper stuffing-grease.) The more intimately a stuffing-grease is divided over the animal fibre, the better it seems to act, and it is for this reason that natural oils and fats are used in conjunction with dégras, which, being in itself an emulsion of water and fats, has the property of emulsifying the added natural oils and fats and distributing them in the fibre. The same object is arrived at by employing wool grease. As the fatty materials are exposed to the air in a state of extremely fine division, oxidation of the unsaturated compounds takes place readily.

The absorption of the stuffing-grease by the fibres tends, at the same time, to increase the weight of the leather (" nourish " the leather).

Compositions which are applied to belts in order to prevent them slipping consist of mixtures of rosin and rosin oil, fish oils, wool fat, castor oil and tallow.

4. CURRIERS' GREASE

French—*Graisse de corroirerie*

The excess of stuffing-grease which has not been absorbed by the leather is scraped off by hand; sometimes it is even " boiled " off the leather by immersion in hot water. The product so obtained is known as " Curriers' grease."

Crude curriers' grease contains fibres from the skin and other impurities, in addition to those originally contained in stuffing-grease. The crude grease is purified, either by melting over water and subsidence, or by hot-pressing in a hydraulic press.

If the original stuffing-grease consisted of fairly good tallow and whale stearine, then the commercial curriers' grease obtained from it (" curriers' hard grease ") represents a light brown mass, containing small amounts only of unsaponifiable matter and of free fatty acids. Such greases can therefore be employed, and are indeed employed, in the manufacture of low-class soaps. If, however, the original stuffing-grease contained a large amount of unsaponifiable matter from whale grease, or considerable quantities of fish oils and whale oils, then the proportion of oxidised acids and unsaponifiable matter is, of course, high. Such inferior curriers' greases are therefore entirely unsuitable for soap-making and are sold as " animal grease," or, if the consistence be very soft, as " animal oil " (see p. 425).

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[1] Lund (English patent 19,495, 1906; German patent 195,410) claims the admixture of glutin or albumen to stuffing-greases. H. Schowalter (French patent 357,525) protects a mixture of ordinary fish oil with a caoutchouc solution in oil of turpentine and aniline oil.

[2] French patent 417,810.

5. Waste Greases from Leather

French—*Graisses régénérées de cuirs*

These greases are considered here separately from those described under 1. (p. 422), as their composition is not yet completely known.

(*a*) *Extracted Grease from Tanned Skins*

French—*Graisse provenant des cuirs tannés*

During recent years the removal of grease from tanned skins has assumed the dimensions of a large scale chemical operation. Hides and skins, even of the largest size, are now extracted with " benzine " (in hermetically closed square tanks), in a manner simulating the extraction of seeds, etc. (see Vol. II. Chap. XIII.). The composition of the grease from tanned leather has not yet been ascertained. It contains considerable quantities of unsaponifiable matter, and (perhaps in consequence thereof) possesses the property of emulsifying a considerable amount of water.[1] The consistence of this grease is that of a thin salve. The " benzine " used for " degreasing " the leather should distil mainly between 90° C. and 100° C.; small quantities only should distil below or above these limits.[2] With regard to the use of carbon tetrachloride [3] in place of benzine cp. Vol. II. Chap. XIII. A method of degreasing skins, by the action of an electric current in alkaline solution, has been patented by *Lehmann.*[4] Other methods have been patented by *Deroy.*[5] In order to purify these extracting greases *Colletas* [6] extracts the skin with a volatile solvent, filters the solution in the hot and evaporates off the solvent. The resulting crude fat is brought to a temperature of 100° C. and treated with an oxidising mixture (alkaline permanganate, chromic acid, nitric acid or hydrogen peroxide).

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[1] Private communication from J. T. Wood.

[2] Trotman, *Journ. Soc. Chem. Ind.*, 1906, 1202.

[3] Cp. French patent 373,681.

[4] German patent 213,174; cp. also Hatschek, *Journ. Soc. Chem. Ind.*, 1910, p. 125.

[5] French patent 11,702.

[6] French patents 394,201, 412,500.

(*b*) *Grease from Wash-Leather Cuttings*

French—*Graisse provenant des rognures de peaux*

Wash-leather cuttings and clippings from tawed skins, which are worked up for the manufacture of glue, contain considerable amounts of grease which must be removed from the solution of gelatin. The cuttings are submitted to a preliminary steeping in lime water, whereby a portion of the free fatty acids is converted into lime soap. The steeped clippings are then boiled up with water, when the grease rises to the top as a scum, which can be readily skimmed off. The crude grease is boiled up with sulphuric acid to decompose the lime soap. The mixture of free fatty acids and neutral fat which rises to the top is sold for making low-class soaps—especially on the Continent—under the name of " Leimfett," " Sudfett."

(*c*) *Grease from Leather Refuse*

French—*Graisse provenant de débris de cuirs*

Owing to the rise in the price of fats in 1907 attention was directed to the fat contained in leather clippings. The cuttings of leather from tanneries and boot factories were extracted with petroleum ether before they were converted into manure, or (prussiate) char. According to *Löb*[1] sole-leather is practically free from fat, whilst " uppers " contain from 8 to 28 per cent ; leather made from horses' hides contains much less fat than do calf skins. The waste leather chips (" Blanchierspäne ") obtained on dressing the stuffed and finished leather contain up to 40 per cent of fat.

The greases recovered by extracting clippings with petroleum ether are dark brown or black, and would compare in this respect with " animal greases " or animal " oils." They may be identified by their unpleasant, tan-like odour. They invariably contain considerable amounts of unsaponifiable matter and free fatty acids. These products are worked up in the same manner as " animal oils " and " animal greases " are treated, namely, by acidification and subsequent distillation.

Similar to these fats, but usually of a better colour, are the fats recovered in the process of glue-making, some figures of which are given by *Bouchard*.

	Minimum.	Maximum.	Mean.
Free acids expressed in oleic acid (per cent)	27	70·7	50·3
Saponification value	193·9	202·2	198·7
Iodine value (Wijs)	51·3	59·2	54·8
Unsaponifiable matter (per cent)	0·92	4·80	2·38
Titer test, ° C.	33·4	37·4	35·8

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[1] *Chem. Zeit.*, 1906, 935.

C. MIXED WASTE GREASES

1. Fuller's Grease—"Seek Oil"

French—*Graisse de foulon.* German—*Walkfett*

Fuller's grease is the fatty substance recovered from the soap suds which have served for scouring silk, woollen, or cotton (dyed Turkey-red) goods by acidifying the suds with a mineral acid.[1] The fatty mass thrown up by the acid is known in Yorkshire under the name "magma" (or "seek," also "sake"; therefore "seek oil" means fuller's grease) and on the Continent as "poudrette." It is put into bags, and subjected to pressure whilst hot, when the dirt (fibres, etc.), remain behind (as "sud-cake"), whereas the expressed fatty matter is collected in tanks below the press.

The process of precipitating the waste wash water with lime and decomposing the lime soaps with mineral acid is now an antiquated one.

A process for decolorising and purifying the grease obtained from dye and calico printing works, previous to the distillation of the fatty acids, is patented by *N. Planowsky and N. Phillippoff.*[2]

According to the quality of the soap used for scouring the goods (and, in the case of grease from woollen mills, according to the quality of wool oil that has been used in the preparing of the wool), the quality of fuller's grease will vary; hence the uses to which fuller's grease is applied also vary. Thus, the suds from silk scouring or best woollen goods, for which olive oil soap has been used, will yield almost pure fatty acids, which may be converted into soap without further purification, whereas the suds from the lowest union goods contain considerable quantities of mineral oil or other hydrocarbons and dirt. Therefore such crude grease must be purified by distillation. The distilled product so obtained is separated into "stearine" and "oleine"; the latter is used as wool oil, or (on the Continent) for soap-making purposes (p. 333). An intermediate quality of fuller's grease is prepared by purifying the crude material by filtration. This material is likely to contain mineral acid.

The commercial examination of fuller's grease is identical with that of wool oils (p. 103).

2. Black (recovered) Oil

French—*Huile noire.* German—*Blacköl, Tuchöl, Extraktöl, Pressöl*

This oil is expressed or extracted from the greasy waste of woollen mills, which is collected from underneath the carding and scribbling machines. Its composition is almost identical with that of the oil employed for oiling the wool in the carding process, provided lubricating oil is not allowed to become intermixed with it. This oil may comprise, therefore, all gradations from a rancid olive oil, through oleic acid, down to the lowest class of wool oils containing more than 50 per cent of unsaponifiable matter.

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[1] Cp. English patent 23,259, 1899; Ruinat, Belgian patent 210,289.

[2] German patent 212,708.

The recovered oil is usually returned to the manufacturers of low-class wool oils who redistil it and thus obtain a purified wool oil which is used for low-class goods or is blended with other wool oils.

Similar in composition to " black oil " is the oil obtained from used engine cloths, greasy cotton waste, and other grease-laden textile goods. Such material is worked up in special establishments where the fatty matter contained therein is recovered by extraction with petroleum ether, or benzine.[1] If the recovered fat is valuable, the extraction is often done merely for the sake of the oil, the cleaned material being returned to the owner free of charge.

3. GARBAGE FATS

French—*Graisses d'immondices ; graisse de gadoues.*
German—*Kehrichtfette*

Under the name " garbage " fats may be comprised all those fats contained in house and other refuse which does not find its way into the sewers. Such refuse is generally collected by the municipalities and destroyed as soon as possible, the primary object being to remove it rapidly from inhabited areas and dispose of it in a sanitary, or at any rate in the least objectionable manner. The system in vogue in this country, and rapidly superseding the older method of dumping on waste land, is to destroy the refuse in specially designed destructors, after a rough sorting out of tins, iron pots, old leather, etc., has taken place in the destructor works. Thus all putrescible matter, together with the fat present, is destroyed, the waste gases being used for heating steam boilers, the steam from which is usually employed for generating electricity (or for providing the necessary steam for sewage works operated in conjunction with destructor works). The refuse (hard burnt clinker) is broken up and used as stone or gravel or sand in concrete-making or is disposed of for cement-making.

As in the foregoing process all the fat is destroyed, efforts have not been wanting to recover the fatty matter. In the United States of America[2] especially methods for the disposal of garbage have been developed. An early process (operated in Buffalo in about 1885) consisted in extracting the garbage with benzine. This process has, however, been superseded by cheaper processes comprised under the term " reduction processes." These processes closely simulate the methods described under " Menhaden Oil " (Vol. II. p. 421) and Slaughter-House Greases (Vol. III. p. 422).[3]

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[1] Cp. S. G. Hall, English patent 10,156, 1904 ; E. Ridgill, English patent 15,231, 1905 ; C. R. Mayo, English patents 8600, 1909 ; 13,340, 1911 ; Belgian patent 246,374.

[2] Cp. *Journ. Soc. Chem. Ind.*, 1908, 376-383.

[3] Cp. S. E. Wilson, United States patent 709,384 (1902) ; German patent 149,551. Edson Reduction Machinery Company, English patent 7519, 1903 ; United States patent 739,998 ; English patents 22,241, 22,242, 1905 ; 19,727, 1906. Wiselogel, United States patent 857,372 (1907). C. S. Wheelwright and J. T. Fiske, English patents 2561, 1903 ; 14,482, 14,483, 14,484, 14,709, 1904 ; 8924, 1907 ; German patents 165,576, 199,945 ; Wheelwright, United States patent 925,970, 925,971 ; Poullet, French patent 368,654.

The best known process, worked in several cities of America by private enterprise (in Cleveland, however, the municipality has a reduction plant) is the *Arnold-Egerton* process, in which the extraction of the fatty matter is performed by purely mechanical means. The garbage, after a preliminary sorting out of tins, etc., etc., is delivered into large digestors, holding about 8 tons, in which the mass is boiled up with steam (" cooked "). When filled, these are screwed down and the mass is " cooked " at 80 lbs. pressure, for a length of time which varies with the material and with the seasons. The vapours escaping through a vent are condensed by a jet-condenser and the condensed water is run into the sewers. After the steam is turned off a separation into three layers takes place. At the bottom collects the solid matter " tankage " ; over this rests an aqueous layer on the top of which floats the separated grease. The grease is taken off and sold for the manufacture of low-class soaps, etc. It is, as a rule, of a dark brown colour ; its composition is that of a low-class grease containing a considerable amount of free fatty acids and also unsaponifiable matter. The tankage is run into special " forms " made of sacks and rags. These are subjected to hydraulic pressure, whereby adhering grease is expressed, together with the water. The water and grease are conducted to settling basins, where the grease separates. The press residue is heated in dryers, ground and screened, and sold as low-grade manure.

4. SEWAGE FATS

French—*Graisses d'eaux d'égouts ; graisse d'eaux-vannes.*
German—*Abwasserfette*

Sewage water (French—*Eaux d'égouts* ; waste water from households, abattoirs, etc.) contains fatty matter in the form of soap, unsaponified fat, free fatty acids, and unsaponifiable matter. As sewage water is of an extremely putrescible nature, sanitary conditions require its immediate removal (from houses, etc.), and both rapid and careful treatment at the sewage works, so as to render the effluent innocuous. The proper disposal of the objectionable matter offers one of the most difficult problems which confront municipalities, as the cost of such disposal must naturally play a very important part in the selection of that method which is best adapted to local conditions. The full consideration of these methods falls outside the scope of this work ; here we can only deal with this subject from the point of view of the fat recovery.

Up to about a decade ago no attempt had been made to recover the fatty matter. In the precipitation processes, which are employed to a great extent, the fatty matter is deliberately wasted, and one of the chief features of the biological (" digestive ") processes is to destroy the fat as completely as possible by making it serve as a foodstuff to the bacteria which digest the fatty matter contained in raw sewage.[1]

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[1] Cp. Lacombe, *Rev. d'Hygiène*, 1906, 817 ; W. J. Dibdin, *The Surveyor and Municipal and Country Engineer*, 1909.

During the last decade, however, experiments have been made, on a large scale, with a view to recovering the fatty matter contained in the sewage. Most of the recovery processes are designed on the lines of the methods practised in the wool, cotton, and silk industries (see pp. 443, 448), and especially in the recovery of wool grease from wool scourers' suds.

The first step was naturally directed to the economical treatment of the fatty matter which separates as " scum " or " sludge " on the top of the sewage water. A large number of devices (strainers, scum troughs, baffle-plate apparatus) are patented, all having for their object the effective separation of the scum from the bulk of the water.[1] A number of inventors attempted the extraction of this scum (and even of raw sewage [2]) with solvents. Processes of this kind were, however, bound to lead to failure, as the fatty matter, which was present to a great extent in the form of soap, gave intractable emulsions. Such a process was tried by the Bradford Corporation on a large scale, but has been abandoned. An apparatus for the extraction by means of solvents has been patented by *Livingston*.[3]

In order to overcome the difficulty caused by the formation of soap emulsions *Heimann* [4] treats sewage sludge in the wet state simultaneously with sulphuric acid and benzine. Laboratory experiments made by *Bechhold and Voss* [5] on a semi-large scale showed that the total amount of fat contained in sewage can be recovered by *Heimann's* method, but experiments on a large scale have not yet been made to demonstrate that this is a workable process.

Other inventors direct their attention to the obtainment of the fatty matter in a solid form. With this object in view, both precipitation by lime and separation by means of acid have been recommended, and (to some extent) tried on a large scale.[6] The recovery of the fatty matter from sludge precipitated with lime [7] is (in the author's opinion,[8] based on practical experience) not likely to lead to adoption. An " acid process," patented by *Maschinenbau-Aktien-Gesellschaft vorm. Beck und Henkel*,[9] was worked on a large scale in the township of Cassel

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[1] W. Wunsch, German patent 123,536 ; J. Ashdown, English patent 9115, 1899 ; Kremer, English patent 14,603, 1901 ; German patent 126,672, 1901 ; English patents 23,670, 1905 ; 24,030, 1905 ; Verwertung Städtischer Abfälle G.m.b.H., German patents 149,551, 153,330, 153,331, 157,372 ; Gesellschaft f. Abwasserklärung, m.b.H., German patents 126,672, 1901 ; 168,305, 1905 ; 172,959, 175,218, 1905 ; French patent 393,172 ; English patent 17,244, 1908 (J. W. Liversedge) ; Bibolini and Baulino, German patent 208,601 ; Nowotny, English patent 24,237, 1908 ; Schumann, German patent 222,207 ; Marchell and Garvie, English patent 3065, 1911 ; E. Merten, German patent 155,561 ; Crosfield and K. E. Markel, English patent 5108, 1905 ; R. Schilling, English patents 14,461, 1903 ; 2073, 1910 ; French patent 412,183 ; A. E. Anderson, German patent 200,570.

[2] Cp. Vial, German patent 141,203.

[3] English patent 12,234, 1910 ; cp. also Testrup, English patent 3247, 1911.

[4] German patent 145,389, 1902.

[5] *Zeits. f. angew. Chem.*, 1908, 1317. Cp. Tillmans, *ibid.*, 1908, 2371 ; Bechhold and Voss, *Gesundheits Ingenieur*, 1908 (31), 742.

[6] For a process aiming at the saponification of the sewage fat by means of alkalis cp. German patent 159,170 (F. Kaeppel).

[7] Cp. French patent 382,555 ; United States patents 889,339, 889,340 (F. and C. Shuman).

[8] Cp. also Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1903, 70.

[9] German patent 135,313.

(Germany). In this process the sewage water was treated with a mineral acid in a manner similar to that employed in the recovery of wool grease (p. 449). The separated sludge containing free fatty acids, etc., was pressed, dehydrated, and extracted with solvents. A specimen of the extracted fat had, according to the patentees, the following composition:—

Free fatty acids	70·8	per cent.
Neutral fat	17·6	,,
Unsaponifiable matter . . .	11·6	,,

This process also has been abandoned.

In a more recent process by *Peter Spence and Sons*,[1] the raw sewage is treated with aluminoferric cake, and the precipitate is made to "curdle," so that it can be easily pressed to a sludge-cake containing about 40 to 50 per cent of water. This sludge-cake is treated with sulphuric acid, and, after suitable treatment of the mass, the fat is extracted with solvents. The crude sewage fat obtained by this process is converted into "oleine", and "stearine" by distillation and subsequent expression. Processes aiming at the separation of a solid cake of sludge by means of centrifugal force have been patented by *Grossmann*.[2]

A process aiming at the direct distillation of sewage sludge by driving off the water at a low temperature, and then distilling off the fatty matter by superheated steam, was patented by *J. Garfield*.[3] It is obvious that a process of this kind cannot lead to satisfactory results. The idea underlying this method has, however, been worked out by *Grossmann* [4] to a process,[5] the essential features of which are the following: The fatty matter is first separated by mineral acid, and the mass so obtained is filter-pressed, whereby the amount of water is reduced to 30 to 40 per cent. The sludge thus obtained is fed into a number of D-shaped retorts, where the water is driven off and the fatty matter is distilled over by superheated steam. Large quantities of butyric acid and other organic acids are obtained simultaneously.

The composition of "sewage fats" must vary with the localities whence they originate. Owing to the exceedingly favourable condition for the micro-organisms [6] thriving in raw sewage, the bulk of the neutral fat discharged into the sewage is hydrolysed; therefore "sewage fats" are characterised by large proportions of free fatty acids. The amount of unsaponifiable matter is also considerable. The nature of the unsaponifiable matter has not yet been investigated. Probably it consists to a large extent of coprosterol, which forms an important constituent of excrementitious matter.

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[1] English patents 12,124, 1900; 8248, 1903; 23,640, 28,646, 1904; 8347, 1905.

[2] English patent 24,483, 1908; German patent 234,807.

[3] English patent 25,876, 1902; cp. also Valentine, *Journ. Soc. Chem. Ind.*, 1910, 244.

[4] *Journ. Soc. Chem. Ind.*, 1905, 655; *ibid.*, 1912, 3; and 1915, 588; cp. also Testrup, Rigby & Andrew, and Wetcarbonising, Ltd., English patent 16,800, 1913.

[5] English patent 29,558, 1904 (The Mayor and Aldermen and Citizens of Bradford, J. Garfield, and J. Grossmann); English patent 16,397, 1908 (J. Grossmann); addition 28,434, 1910.

[6] E. de Kruyff proposes for the micro-organisms the term "lipobacteria" (*Bull. Dep. Agr. aux Ind. néerl.*, 1907, 9).

Examinations made recently by *König and Schluckebier*[1] show that the fat in excrements obtained from animals fed with peas, milk, potatoes, maize, coconut cake and milk, coconut and sesame cake, and meat powder, contained in the same order the following amounts of unsaponifiable matter: 25 per cent, 25·8 per cent, 30·5 per cent, 6·16 per cent, 10·44 per cent, 15·5 per cent, and 20·36 per cent. In all cases the bulk of the unsaponifiable matter consisted of coprosterol, with smaller quantities of phytosterol or (and) cholesterol, according as to whether the food was of vegetable or animal origin (or was composed of both animal and vegetable matter). The extraction of fatty matter in animal faeces with CCl_4 yields in twelve hours 17·9 to 33·8 per cent more fatty matter than with dry ether in twenty-four hours.[2]

Judging from the composition of sewage fats it is evident that at present the products cannot pay the expenses of the process, unless, indeed, the recovery of the fat form an integral part of the sewage disposal process. Some exaggerated statements regarding the value of some of the above-described recovery processes must be accepted with the greatest reserve. The author is of the opinion that under present conditions the recovery of the fat merely for the sake of this product alone cannot be a profitable process. The efforts of inventors should therefore aim at dovetailing a fat-recovery process into the system of the obligatory sewage purification. If the problem be considered in that light, there is a prospect of arriving at a satisfactory method of fat recovery in a practically complete and relatively economical manner.

2. Waste Waxes

WOOL FAT, WOOL GREASE, "RECOVERED GREASE," "BROWN GREASE"[3]

French—*Suintine*; *graisse de suint.* German—*Wollfett, Wollschweissfett.* Italian—*Grasso di lana greggio*; *sugna*

The occurrence of wool fat, the proportions contained in natural wools, and some other technical notes have been given in Vol. II. p. 900. In this section the practical aspect of the problem of working up wool-scourers' suds on a large scale will be considered somewhat more fully, although a complete enumeration of the not inconsiderable number of patents which have been taken out during the last fifty years must fall outside the scope of this work.[4]

The older method, which was especially in vogue on the Continent, was to run the waste suds into large cisterns and to treat them with lime, when a heavy precipitate, consisting of neutral esters, lime salts of fatty acids, carbonate of lime, and caustic lime was obtained. This precipitate, known as "suinter," was dug out (or passed in a state of suspension through filter-presses in order to remove the bulk of the water) and dried by exposure to the air. The "suinter" was then subjected to dry distillation in iron retorts for the production of an illuminating gas ("Fettgas"). As the excess of lime proved very troublesome, an improvement was introduced by precipitating the wash-waters with calcium chloride or magnesium chloride.

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xv. 653; cp. also J. Long and W. A. Johnson, *Journ. Amer. Chem. Soc.*, 1907 (29), 1214; R. Inaba, *Biochem. Zeits.*, 1908, 355.

[2] A. D. Emmett, *Journ. Amer. Chem. Soc.*, 1909 (31), 693.

[3] In the United States this grease is known as "dégras"; "English dégras"; "German dégras."

[4] Cp. Langbeck, *Journ. Soc. Chem. Ind.*, 1890, 356. J. M. Baudot, Austrian patent Applic., A. 3126 (1906); French patent 413,442; E. Dowie, United States patent 892,370 (1908).

This treatment aimed, however, more at a purification of the suds—before they were allowed to run into the river courses—than at a recovery of the wool grease.

After the valuable properties of wool wax had been rediscovered (*O. Braun, O. Liebreich*), endeavours were made to extract the "suinter" (or even the raw wash-waters)[1] with solvents.[2] But the troublesome emulsions which were formed, and the costliness of the processes,[3] led to the abandoning of these attempts. At present precipitation with lime has been superseded by the treatment with mineral acid, much as the precipitation with lime in the recovery of fuller's grease has been substituted by the treatment with mineral acid (p. 443).

Much more satisfactory results were obtained by treating the wool-scourers' suds with calcium, magnesium, or iron salts, etc., when the precipitated salts of fatty acids carried down with them the neutral portions of the wool fat. The precipitate was then extracted with acetone,[4] in which the neutral portions only were stated to be soluble. But not only did part of the soaps dissolve in acetone, but there were obtained simultaneously troublesome emulsions, which rendered these processes also unworkable[4] on a large scale. According to a recent patent the wool-scouring liquors are treated with a solution of magnesium sulphate and heated under a pressure of 125 lb. per square inch, whereby it is claimed a complete separation of the soap and grease is obtained.[5]

More success attended a mechanical process which was practised for some time on a manufacturing scale. It consisted in passing the suds through a centrifugal machine, when a turbid soap solution ran off, whereas the wool wax remained behind. The soapy solution was then treated ("cracked") with mineral acid to recover its fatty acids, or was evaporated down and calcined for the recovery of the potash in the waters. The crude wool wax in its turn was purified by pressing in a hydraulic press or by boiling up with water, allowing to settle out, and then kneading repeatedly with water until a fairly pure product was obtained. The resulting wool wax was dark yellow, and as all attempts to bleach it led to unsatisfactory results, it was intermixed with about 20-25 per cent of water, in order to obtain a lighter-coloured product. This was brought into commerce under the name "lanolin." The anhydrous product is obtainable in commerce as "adeps lanæ."

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[1] Cp. French patent 368,654.

[2] Cp. German patent 42,172 (A. v. Rad).

[3] Cp. German patent 38,444.

[4] H. Breda recommends to replace acetone by the higher boiling ketones (boiling point 67° to 167° C.). Cp. English patents 8588, 1903; 17,656, 1906; German patents 181,400, 181,401; cp. also Chatelan and Spiesz's German patent 194,871, which claims the admixture of inert substances to the lime salts before extracting them with solvents.

[5] F. E. Underwood and B. F. Ilston, United States patents 1277, 784, 1918.

With the improvements in the design and efficiency of centrifugal machines the mechanical method for the separation of wool wax from the soapy liquors is coming more into vogue.[1] Some success attended the precipitation of the grease by treatment with carbonic acid (wasted chimney gases) under pressure.[2] *Jean de Raeve* treats the crude liquors with gaseous chlorine. The method generally practised in the Yorkshire woollen mills for the production of Yorkshire grease is as follows :—

The soap suds are collected in large tanks, where dirt, etc., is allowed to subside, and are run or pumped into cisterns to be acidified ("cracked") with mineral acid, when the wool grease, together with the fatty acids from the soap used in scouring, rise to the top. The fatty matter ("magma") is collected by skimming off, allowed to drain on coke beds or other suitable filters, whereby the bulk of water is removed, and then expressed in a hydraulic press in the hot, so as to eliminate the fibres, dirt, etc., that are occluded by the fatty matter. The press cakes ("sud cakes") still retain 15 to 20 per cent of grease, the extraction of which is sometimes remunerative. On account of its proportion of nitrogen (2 to 3 per cent) the cake ("sud cake") is sold for manurial purposes. The acid liquors are run away; they still contain a notable amount of grease in suspension.

In some localities the liquors must be neutralised (with lime) previous to their being discharged into the water-courses.

The composition of a grease of this kind (free from glycerides and mineral oil, and freed from ash) was ascertained by the author, and found to be as follows [3] :—

Volatile acids	1·28 per cent.
Insoluble free fatty acids . . .	20·22 ,,
Combined fatty acids . . .	48·47 ,,
Alcohols	36·47 ,,

The occurrence of *volatile acids* appears to be due to secondary reactions. (*A. and P. Buisine* [4] point to fermented wool-scourers' suds as a rich source of volatile fatty acids, from acetic acid up to caproic acid.)

The free fatty acids consist chiefly of acids occurring naturally in wool grease; [5] the remainder is derived from the fatty acids liberated by the decomposition of the waste soaps by the mineral acid.

The combined fatty acids form with the bulk of the *alcohols* neutral esters (wax). In the example given (Vol. I. Chap. XI.) the proportion of neutral esters amounted to 72·31 per cent. *The alcohols* are partly present as esters (*i.e.* combined with fatty acids to form 72·31 per cent of wax) and partly as free alcohols. In the given example their amount was 6·21 per cent. The methods adopted in the analysis of this grease have been described in Vol. I. Chap. XI.

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[1] W. Kelsey, English patent 123,848, 1918; G. C. Garmain, English patent 118,332, 1917; E. E. Ayres, jun., *Met. and Chem. Eng.*, 1916 (14), 317-318; cp. also E. V. Chambers, *Journ. Soc. Dyers and Colourists*, 1916, 61.

[2] E. V. Chambers, *Journ. Soc. Dyers and Colourists*, 1916, 61.

[3] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 134.

[4] *Compt. rend.*, 1897 (125), 777.

[5] Schulze, *Berichte*, 1872, 1076; 1873, 251; 1874, 571.

The crude wool fat used to be treated with an alkaline solution (ammonia, soda solutions, etc.) when an emulsion of soap and wool wax was obtained. For their separation the emulsified mass was either treated with methyl- or ethyl-alcohol to remove the soaps, whilst leaving the neutral wax, which is insoluble in these solvents, behind; or the mixed soap and wool wax were exhausted with ethyl acetate, in which the wool wax only is soluble. In the former case the raw wool wax was obtained in substance, whereas in the latter process the wool wax was recovered by distilling off the acetic ester.

The crude wool wax and the soap solutions were then further worked up as described above.

In the process of recovery outlined above a considerable amount of fatty matter is lost. Hence many patentees endeavoured to extract raw wool with volatile solvents.[1] The enumeration of these processes falls outside the scope of this work, as they have all been abandoned (at any rate in this country), not only on account of the great fire risk, but also, and perhaps chiefly, because the wool fibre is damaged by the extracting process. (This is no doubt due to the fact that the solvent removes too much of the natural grease, and produces a harsh, brittle fibre which causes too great a waste in spinning.) Two processes which were tried on a large scale may, however, be mentioned specifically. The *carbon bisulphide* process, which was worked for some time in this country in plant designed by *Singer and Judell*,[2] was found especially unsuitable, as a portion of the sulphur which commercial carbon bisulphide contains was taken up by the wool fibre, imparting to it a yellow colour. A process for extracting wool with *petroleum ether* (*G. and A. Burnell*), entailing less complicated plant, was also tried on a large scale, but was not found suitable. At present endeavours are being made to introduce processes for extraction with *carbon tetrachloride*,[3] but as far as the author is aware these have not been carried out hitherto on a large scale.

A process for the recovery of wool grease without the use of mineral acids or solvents was patented by *John Smith and Son, and Leach.*[4] Their method combines the advantageous features of some of the foregoing processes, and would seem to commend itself from a purely sanitary point of view from the fact that no effluents which pollute the river courses are obtained. The wool-washing liquors are concentrated in multiple vacuum apparatus [5] (which was first used for this purpose by *Langbeck*) until a concentrated lye of the specific gravity 1·23 is obtained. This liquor has a viscous consistence, and solidifies when cold. It is run, whilst still warm, through a centrifugal machine, when the soap liquor (containing the potash salts originally occurring in the wool, as also the soaps used in scouring the wool) runs off. The liquor is further concentrated, and finally calcined in a revolving furnace. Thus the potassium originally contained in the wool, together with the alkali introduced in the form of soap in scouring the wool, is recovered as carbonate. It will thus be seen that in this process the free fatty acids of the wool grease, as also the fatty acids introduced as soap in the scouring of the wool, are lost. The wool grease is worked up, in the manner described above, into " lanolin," or sold as " adeps lanæ."

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[1] Mayo, English patents 8600, 1909; 17,125, 1909; 22,615, 1909.

[2] *Journ. Soc. Chem. Ind.*, 1889, 24.

[3] Cp. Bernard, English patent 28,364, 1907; F. and C. Shuman, United States patents 889,339, 899,440.

[4] English patent 15,131, 1898; German patent 113,894.

[5] Cp. Lewkowitsch, "Evaporation *in vacuo* of Solutions containing Solids," *Journ. Soc. Chem. Ind.*, 1905, 1149.

For a process, suggested by *Spiess and Chatelan*, to treat wool-scourers' wash-waters without using a vacuum, the reader must be referred to the original paper,[1] as the process appears to have been worked hitherto only on an experimental scale. It need therefore only be pointed out that the patentees mix the wash-waters with toluene and heat the mixture when, at a temperature of 80°-82° C., toluene and water pass over. The vapours are condensed fractionally, so that the water and toluene are obtained separately. The toluene is then used again, and thus serves to evaporate off an indefinite quantity of water.

With regard to processes aiming at the saponification of wool wax cp. p. 411.

Crude wool grease is used as a lubricant, with or without admixture of mineral oils (see " Wool Oils," p. 103), further as a dégras substitute (see p. 431), and as a stuffing-grease (see p. 439), especially in the United States of America. It is unsuitable for the manufacture of soap. The production of wax-like bodies for use in the paint and varnish industries by treating crude wool fat with air in the presence of basic substances at high temperatures has been patented by *Lifschütz*.[2]

A solution of wool fat in a chlorinated hydrocarbon has been used for coating iron work as a rust preventive.[3]

The commercial products obtained from wool grease in the manner indicated above are *wool wax* and *wool fat fatty acids*.

The bulk of wool grease is, however, distilled, whereby distilled grease is obtained.

Proposals have been made to hydrogenate [4] the crude wool fat and also to employ the *Varrentrapp* reaction.[5]

Wool Wax

Neutral wool wax prepared by any of the methods described above is used both in its hydrous (" lanolin ") and in its anhydrous state

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[1] *Zeits. f. chem. Apparatenkunde*, 1908, 1; German patent 194,871 (Spiess and Chatelan); cp. German patent 163,444 (Stöhr and Co.).

[2] German patent 234,502.

[3] O. Reynard and E. Edser, English patent 163,474, 1920.

[4] W. Schrauth, *Seifenseider-Zeit*, 1916 (43), 437-8; C. Ellis, United States patent 1086, 357.

[5] W. Schrauth, *Seifenseider-Zeit*, 1916 (43), 437-8.

(" adeps lanæ ") as a basis for ointments,[1] salves, and cosmetics (cp. Vol. II. p. 906). Smaller quantities are employed as " super-fatting " agents in the preparation of toilet soap (cp. this Vol. p. 345). The chemical examination of these products embraces the determination of water, ash, and free acids, as also the detection of foreign substances. The readiest means of detecting the latter is supplied by determining the chemical and physical characteristics of the sample, whereby the direction which further examination should take will be indicated. Presence of glycerol would point to admixture with glycerides or glycerin. A detailed examination of the unsaponifiable matter would reveal the presence of paraffin wax or other hydrocarbons. (It should be remembered that wool wax must be saponified with alcoholic potash under pressure, or with sodium alcoholate.)

A somewhat detailed examination of a wool wax carried out by the author [2] is given in Vol. I. Chap. XI.

The efforts of several inventors (*Jaffé and Darmstädter*, *Ekenberg and Montén*) were directed to the separation of wool wax into several fractions. Thus *Ekenberg and Montén* [3] prepared by centrifuging or expressing wool wax at a temperature of 30°-35° C., three fractions described as " Cholaïn," " Cholepalmin," and " Cholecerin." The melting points of these fractions are as follows :—

	Melting Point. ° C.
Cholaïn	25-29
Cholepalmin . . .	37-38
Cholecerin . . .	49-55

Lifschütz [4] found by treating (wool fat, or, preferably) wool wax with bone char in petroleum ether solution that the wool wax can be resolved into two portions, one of which is retained by the bone char, whereas the other remains dissolved in the petroleum ether solution. The residual waxy matter obtained after distilling off the solvent differs from the original wool wax in that it has practically lost its power of emulsifying water. The waxy portion retained by the char can be extracted by means of alcohol, chloroform, carbon tetrachloride, ether, acetone, carbon bisulphide, or even by petroleum ether containing 5-10 per cent of alcohol,[5] or by means of solutions of oils and fats (olive oil, lard oil [6]). This constituent of wool wax exhibits a much higher water-emulsifying power than does the original (wool fat or) wool wax. (The process of resolving into two different constituents can also be carried out with wool fat fatty acids or with products containing wool fat.[7]) The portion retained by the char is brought into commerce under the name of " lanogene." [8] The admixture of 1 part of this to 99 parts of vaseline [9] is stated to cause the mixture to absorb 200 parts of water, and an admixture of 2 or 3 parts increases the power of absorbing water to 300 parts. "Lanogene" is said to be suitable as a basis for ointments, salves (cp. Vol. II. p. 942), and emulsions prepared with the aid of mineral waxes; also emulsions of oils and fats with water.[1]

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[1] Cp. P. G. Unna, *Monatsh. f. prakt. Dermatologie*, 1907.

[2] See Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1896, 14.

[3] German patent 81,552.

[4] German patent 163,254.

[5] German patent 178,804.

[6] German patent 185,987.

[7] German patents 171,178, 185,987, 190,959.

[8] German patent 167,849.

[9] Such and similar mixtures are brought into commerce under various fancy names (" Euvaseline," " Eucerin," etc.).

Wool Fat Fatty Acids

As a by-product in the manufacture of "lanolin" or "adeps lanæ," soap solutions are obtained which contain the fatty acids originally occurring in the wool fat, as also the fatty acids introduced as soap in the scouring of the wool. In some of the processes mentioned above the soapy liquors are only worked up for the recovery of potash, it being considered unremunerative to recover the fatty acids (the latter serving in the calcining process merely to facilitate the destruction of the organic substances).

In some works the fatty acids are recovered from the soapy liquors by treatment with mineral acid ("cracking").

A sample of fatty acids so obtained was examined by the author with the following result:—

Acid value	184·5
Saponification value	203·4
Unsaponifiable+unsaponified matter	3·54 per cent.
Unsaponifiable	1·23 ,,

These fatty acids are made into soap or into lubricating grease (see Chap. XV. "Solidified Oils"[2]), or (as a substitute for boiled oil) into paints.[3] For the latter purpose the free fatty acids are converted into magnesia soaps, which are dissolved in crude wool wax and mixed with a rosin soap, such as zinc rosinate.

Rosin in presence of wool fat acids can be detected and determined quantitatively by *Twitchell's* method.

The mixture of magnesium salt and wool wax may, of course, be prepared by precipitating wool wash-water with a magnesium salt (with the addition of a little lime).

The magnesium salts of wool fat fatty acids are soluble in tar oils and mineral oils.[4]

Distilled Grease

When "recovered grease" is subjected to distillation[5] with superheated steam, a light oil, consisting of hydrocarbons, is obtained first; then follow heavier fractions, which separate, on cooling, into a liquid and a solid portion. The higher distillates are treated much in the same way as are distilled fatty acids in candle-works, so that the following products are finally obtained: "oleine," chiefly used as wool oil, and

[1] Cp. S. Knopf, English patent 17,523, 1907; W. Loebell, German patent 169,491.
[2] Cp. also Donath, *Chem. Zeit.*, 1899, 62; Rosengren, *ibid.*, 1899, 382.
[3] German patent 166,563; English patent 6502, 1902.
[4] Joske, German patent 241,565.
[5] Cp. United States patent 896,093 (C. Ellis).

"stearine," employed as a "sizing tallow" or "stuffing-grease," and as inferior material in the candle and soap industries.

The changes the "recovered grease" undergoes in the distillation [1] consist in the hydrolysis of the neutral esters, whilst concurrently another portion of the compound esters is broken up into fatty acids and hydrocarbons, the latter being formed in consequence of the fatty acids assimilating all the available oxygen in the molecule. This is illustrated by the following equation:—

$$\underset{\text{Cetyl palmitate.}}{C_{15}H_{31}CO\,.\,O\,.\,C_{16}H_{33}} = \underset{\text{Palmitic acid.}}{C_{15}H_{31}CO\,.\,OH} + \underset{\text{Cetene.}}{C_{16}H_{32}}.$$

A portion of the neutral esters is carried over undecomposed by the current of steam, and is found as such in the "distilled grease."

The free alcohols in the "recovered grease" partly distil over as such, whilst another portion is broken up into hydrocarbons with loss of water. Cholesterol, when subjected to distillation, is known to yield hydrocarbons (cp. Vol. I. Chap. III.).

Part of the fatty acids distil over undecomposed, whilst another portion, in their turn, are converted into hydrocarbons; this holds especially good of those fatty acids which easily undergo dehydration.

The examination of "distilled grease" embraces the determination of *free fatty acids*, *neutral esters* (*waxes*), and *unsaponifiable substances*. The latter consist chiefly of hydrocarbons, which have been looked upon frequently as mineral oil (cp. "Wool Oils"). The nature of these hydrocarbons is but very imperfectly known; being derivatives of cholesterol, they exhibit optical activity.

This has been first shown by *Lewkowitsch*, who observed the optical activity of the distilled grease hydrocarbons in 1894 and then again in 1897, when the first and second editions of the present work were prepared.[2] Later on the optical activity was recorded by *Gill and Mason* [3] (whose numbers are given in the following table) and afterwards (see below) by *Marcusson*.[4] [The latter put forward the conjecture [5] that the optical activity of natural petroleums is due to hydrocarbons generated from the cholesterol contained in animal oils and fats which underwent conversion into petroleum (see Vol. I. Chap. I.). This conjecture has been amplified by *Engler* (see Vol. I. Chap. I.). For a discussion of this conjecture and its bearing on the theory of the origin of petroleum, which falls outside the scope of this work, compare the papers given in the footnote.[6] It may be added that *Molinari and Fenaroli* [7] arrived at the conclusion that the optically active substances in petroleum do not yield an ozonide, and hence do not consist of cholesterol; since the same authors showed that phytosterol yields an insoluble ozonide, their conclusion may be amplified by stating that the optical activity of petroleums cannot be ascribed to the presence of phytosterol.]

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 142.

[2] Through an oversight the actual polarimetric readings have not been published, the statement merely being made in the first two editions that these hydrocarbons, being cholesterol derivatives, will exhibit optical activity. Cp. German Edition, 1904, vol. ii. p. 732.

[3] *Journ. Amer. Chem. Soc.*, 1904, 665.

[4] *Mitt. Königl. Materialprüfungsamt*, 1904.

[5] *Chem. Revue*, 1905, 4.

[6] Engler, *Petroleum*, 1907, 849; Lewkowitsch, *Jahrbuch d. Chem.* 1908 (xviii.), 416; Engler, *Zeits. f. angew. Chem.*, 1908, 1585.

[7] *Berichte*, 1908, 3704.

In an examination of a distilled grease oleine the mass was boiled out repeatedly with alcohol. The insoluble portion was judged to consist of hydrocarbons, inasmuch as it was insoluble in acetic anhydride. On distilling the insoluble portion *in vacuo* three fractions were obtained. They all had the smell which crude paraffin oils of the same boiling point possess. Some properties of these products are set out in the following table (*Lewkowitsch*)[1]:—

Fraction.	Appearance.	Specific Gravity at 80° F. compared with water at 80° F.	Iodine Values.
1st	Clear, bright yellow oil; exhibiting bloom .	0·8513	71
2nd	Bright oil, partly solidifying on cooling; exhibiting bloom.	0·9162	74
3rd	Darker oil; solidified on cooling; exhibiting bloom.	0·9180	61
4th	Residue	...	71·7

Gill and Forrest[2] examined the unsaponifiable matter from distilled wool oleine by removing the cholesterol with acetic anhydride and subsequently distilling the residue *in vacuo*. The fractions were recrystallised from acetone. From the determination of the molecular weight and iodine absorption these authors conclude that the hydrocarbons in distilled grease oleine belong to the olefine series.

Marcusson and Skopnik[3] have found for the unsaponifiable matter iodine values ranging from 51 to 79 and specific gravities 0·900 to 0·917 at 15° C.

The distilled grease hydrocarbons give, in contradistinction to hydrocarbons derived from petroleum, the isocholesterol reaction. For the detection of mineral oils in wool grease oleine *Settimj*[4] recommends as a solvent a mixture of one part of amyl alcohol and two parts of 96 per cent ethyl alcohol and proceeds as follows:—10 c.c. of the sample are shaken with 40 c.c. of the mixed alcohols when even 5 per cent of mineral oil will show an oily layer separating on top.

Winterfeld and Mecklenburg[5] recommend a mixture of methyl and ethyl alcohols. These authors also recommend this test for the detection of rosin oil.

In view of the fact that *Engler* obtained by the distillation of cholesterol hydrocarbons which still showed a proportion of 1·2 to 2 per cent of oxygen (as against 4·3 per cent in cholesterol), some doubt must be entertained as to whether the above-described substances consisted entirely of hydrocarbons, their elementary analysis not having been carried out.

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[1] *Journ. Soc. Chem. Ind.*, 1892, 141.
[2] *Journ. Amer. Chem. Soc.*, 1910, 1071.
[3] *Zeits. f. angew. Chem.*, 1912, 2577.
[4] *Ann. Lab. Chim. Centr. delle Gabelle*, 1912, 197.
[5] *Mitt. Königl. Materialprüfungsamt*, 1910, 471.

The methods applicable in the exhaustive examination of distilled grease have been fully described in Vol. I. Chap. XI.

The commercial analysis of **distilled grease oleine** for oiling wool has been described under "Wool Oils," p. 103.

The following table gives some data ascertained by *Gill and Mason* :—

	Specific Gravity.	Bromine Addition Value.	Bromine Substitution Value.	Optical Rotation.[1]	Refractive Index at 20° C.
Wool fat oleine (A) .	0·896	28·8	14·2	17° 58′	1·4976
,, ,, (B) .	0·902	25·1	14·8	17° 36′	1·4991
,, ,, (C) .	0·896	21·5	16·8	15° 13′	1·4948

The following figures determined by the author show the characteristics of a commercial sample of wool grease oleine :—

Specific gravity at 60° F.	0·8938
Acid value	101·7
Saponification value	103·1
Unsaponifiable matter, per cent	50·31
Specific gravity of unsaponifiable matter . . .	0·8865
Rotation of unsaponifiable matter	+25

Marcusson examined the unsaponifiable matter from French and German oleines, after having removed from it all the substances soluble in acetic anhydride (by boiling out the unsaponifiable matter once or twice with that menstruum).

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[1] Gill and Mason do not state whether the rotation was to the right or to the left.

[TABLE

Portion Insoluble in Acetic Anhydride

		Specific Gravity at 15° C.	Viscosity (Engler) at 20° C.	Refractive Index.	Specific[1] Rotation at 18°-20° C. in (about) 3 per cent Benzene Solution, α_D.
1. Oleine (German), of specific gravity 0·9060, yielding 55 per cent of total unsaponifiable matter	contains paraffin wax (!)	...	...	1·497 (at 18° C.)	+25·9
2. Oleine (German), of specific gravity 0·9065, yielding 53 per cent of total unsaponifiable matter	contains paraffin wax (!)	0·9053	15·6	...	+23·4
3. Oleine (French), of specific gravity 0·9077, yielding 39 per cent of total unsaponifiable matter	contains no paraffin wax (!)	0·9117	20·3	...	+18·1
4. Oleine (French), of specific gravity 0·9036, yielding 42·8 per cent of total unsaponifiable matter	contains no paraffin wax	...	...	1·497 (at 27·5° C.)	+28·0
5. Oleine (French), of specific gravity 0·9035, yielding 41·3 per cent of total unsaponifiable matter	contains no paraffin wax	...	...	1·497 (at 27·5° C.)	+24·5

By distilling 22 grms. of the unsaponifiable portions from wool fat oleine at 0·1-0·2 mm. pressure, *Marcusson*[2] obtained the following fractions :—

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[1] The indications in the heading are contradictory, and therefore prove no more than the fact that dextrorotation was observed.

[2] *Chem. Zeit.*, 1907, 419.

[TABLE

Fraction.	Boiling Point. °C.	Grams.	Rotation[1] in 3 per cent Benzene Solution at about 20° C. α_D.	Iodine Value (Wijs).
I.	150-190	2·6	+ 5·9	75·4
II.	190-210	1·6	+12·3	75·4
III.	210-230	2·3	+21·9	80·8
IV.	230-250	3·3	+29·9	86·3
V.	250-275	3·7	+37·4	84·5
VI.	residue	10·0	+32·0	95·3

Morgenstern[2] patents a process for obtaining the pure alcohols by distilling the crude alcohols in superheated steam under reduced pressure.

Fraudulent admixture of petroleum hydrocarbons and distilled grease oleine is detected by a lower optical rotation and iodine value than are exhibited by genuine specimens.

Distilled grease stearine is a hard, whitish, solid substance, differing in its appearance from commercial stearic acid by the absence of crystalline structure. This stearine is easily identified by its strong isocholesterol reaction (Vol. I. Chap. III.) and by its high iodine value, due to presence of iso-oleic acid. It consists chiefly of free fatty acids, as the bulk of the liquid hydrocarbons has been removed by pressing. In commercial analysis the melting and solidifying points of the stearine, the "saponifiable," and the "unsaponifiable" are required.

The proportion of saponifiable matter is ascertained by boiling an accurately weighed quantity with standardised alcoholic potash, as described under "Saponification Value," Vol. I. Chap. VI. Each c.c. of normal alkali required is taken as corresponding to 0·284 grm. of stearic acid. (The small quantity of neutral esters, if any, in the stearine is thus calculated as stearic acid.) The unsaponifiable matter is determined in the manner described in Vol. I. Chap. VI.; it is most convenient to use for this test that quantity which has served for the determination of the "saponifiable."

The following table gives a few analyses of "distilled grease stearines." The free acid is calculated to stearic acid:—

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[1] It is uncertain whether "specific" rotation or "observed" rotation is meant. It may also be remarked that the quantities in col. III. add up to 23·5 grms.

[2] French patent 421,044; United States patent 991,874.

[TABLE

Solidifying Point.	Melting Point.	Specific Gravity.		Water.	Free Acid.	Neutral Esters.	Unsaponifiable.	Iodine Value.	Observer.
°C.	°C.	At 15·5° C.	At 98° C.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
45	48	0·9193	0·836	0·6	88·6	2·11	0·49	...	Hurst
53·5	57	0·9044	...	1·48	76·3	7·7	0·4	...	,,
...	...	...	...	2·85	72·13	...	3·12	...	,,
41·5	...	...	...	...	98·9	...	...	33·7	Lewkowitsch
...	...	...	...	...	...	...	7·2	...	,,
56·8-59	...	...	...	...	...	...	20-20	...	Coen[1]
41·5-43·5	...	...	...	...	...	...	9-15	...	,,

The residue left in the stills, **wool fat pitch** (goudron), is softer than stearin pitch and melts at about 35° C. It is used as a lubricant for hot neck rollers, as an insulating mass for cables, and for similar purposes[2] for which stearine pitch is used, *e.g.* for the manufacture of impregnating substances for roofing felt. For these purposes the wool fat pitch is blown with air after adding oxidising substances, *e.g.* $MnO_2 + SO_4H_2$, and aldehyde,[3] or by treating wool fat grease pitch with sulphur at temperatures up to 300° C.[4]

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[1] *Ann. Lab. Chim. Centr. delle Gabelle,* 1912, 567.

[2] With regard to the examination of such pitch cp. Donath and Margoschen, *Chem. Revue,* 1904, 194.

[3] Cp. O. Schreiber, German patent 208,378; cp. also Lifschütz, German patent 253,965.

[4] M. F. Malchow Leopoldsboller Dachpappen-Holzzement und Tectolith Fabrik, German patent 225,911.

APPENDIX

VOL. I

Page 1

The oxidation of a hard paraffin wax in the presence of a lead catalyst resulted in the formation of fatty acids ranging from myristic to arachidic acids.[1]

Page 2

The fat extracted from yeast contains, according to *J. S. MacLean and E. M. Thomas*,[2] from 25 to 45 per cent of unsaponifiable matter, the bulk of which is a sterol. Palmitic, oleïc and linolic acids were identified.

Page 7

E. Fischer, M. Bergmann and H. Bärwind[3] propose as a general method for the preparation of monoglycerides the action of acyl chlorides on acetone-glycerol $(CH_3)_2C<\begin{array}{l} O.CH_2 \\ CH.CH_2OH \end{array}$ in the presence of quinoline.

Page 31

By passing a current of phosgene through castor oil at a temperature of 100° C. *A. Piutti and A. Curzio*[4] obtained a product containing 9·03 per cent of chlorine. Since olive, arachis, almond, and sesamé oils when treated in a similar manner yield products containing only 0·08 to 0·18 per cent of chlorine it is assumed that the reaction takes place with the hydroxyl group.

Page 41

P. A. Levene and H. S. Simms[5] have isolated from liver, lecithin, stearic and palmitic acids, and two unsaturated acids yielding stearic acid and arachidic acid on reduction.

Page 52

W. Stokoe[6] shows the effect on butter and margarine of various moulds.

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[1] H. H. Franck, *Chem. Zeit.*, 1920 (44), 309.

[2] *Biochem. Journ.*, 1920, 483 ; cp. also H. Haehn, *Chem. Zentr.*, 1922 (93), I. 506, and English patent 146,431, 1920.

[3] *Berichte*, 1920 (53), 1589 ; cp. also E. Fischer and E. Pfähler, *ibid.*, 1920 (53), 1606.

[4] *Giorn. Chim. Ind. Appl.*, 1921 (3), 214.

[5] *Journ. Biol. Chem.*, 1921 (48), 185, and *ibid.*, 1921 (51), 285.

[6] *Journ. Soc. Chem. Ind.*, 1921, 75 T.

PAGE 74

The method adopted by *Lewkowitsch* for following the course of saponification by means of the acetyl value has been adversely criticised by *J. P. Treub*,[1] who, basing himself on some figures obtained by *Marcusson*,[2] states that the acetyl values found do not measure the amount of hydroxyl in the glycerol radicle, but they refer rather to oxidation products of the fatty acids.

That this view is erroneous is shown by the figures given in the tables, pages 75 and 76, where in the first table, that of tallow saponified with caustic soda, we note the acetyl value of the partially saponified mass was at one period as high as 78·9, whereas that of the total fatty acids was only 8·8. *Treub's* second contention, that the figures given do not fall into a continuous curve rising to a maximum, but instead rise and fall in zigzag fashion, is beside the point, for it cannot be assumed that saponification takes place regularly, and that all the triglyceride is converted first into di- and monoglyceride, and finally into free fatty acid, whereas we shall have in the mixture varying amounts of tri-, di-, and monoglycerides and free acids. This is all the more likely, since the reaction takes place in emulsion where contact between the phases cannot be theoretically perfect. Even in cases where the reaction takes place in solution the fact that hydrolysis proceeds in stages has been shown by *E. Yamasaki* [3] by saponifying triacetin.

The whole theory of saponification is discussed mathematically by *Treub*,[1] who incidentally shows that the number of molecules of a fatty acid combined in a glyceride has a considerable influence on the velocity of saponification when saponification takes place in emulsion.

P. J. Fryer [4] shows that when saponification takes place under the same conditions equal weights of all oils and fats are saponified in a given time. According to *F. E. Weston* [5] the time is materially shortened by the addition to the reacting masses of colloidal clay, although this on a commercial scale will cause considerable difficulty in salting out the soap.

PAGE 127

For two papers describing some new indicators see *Norman Evers* [6] and *F. Carr.*[7]

E. Walker [8] has determined the effect of the sodium salts of fatty acids on the surface tension of water.

PAGE 149

The anhydride of erucic acid melts at 46-46·5° C.[9]

PAGE 162

For a study of the structure of a thin film of palmitic acid on water see a paper by *N. K. Adam.*[10]

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[1] *Journ. de Chimie physique*, 1918 (16), 107.

[2] *Berichte*, 1906 and 1907.

[3] *Sci. Rep. Tohoku Imp. Univ.*, 1920 (9), 451.

[4] *Analyst*, 1921, 87.

[5] *Chem. Age*, 1921 (4), 604, 638.

[6] *Analyst*, 1921, 393.

[7] *Analyst*, 1922, 196.

[8] *Trans. Chem. Soc.*, 1921 (119), 1521.

[9] D. Holde and C. Wilke, *Zeits. f. angew. Chem.*, 1922 (35), 105.

[10] *Proc. Royal Soc.*, 1921, A, Vol. 99. Cp. also P. Woog, *Comptes rend.*, 1921 (173), 387.

PAGE 205

B. H. Nicolet [1] states that the tetrabromide obtained from α-elæostearic is not identical with linolic tetrabromide, but is probably identical with the tetrabromide obtained from the β acid.

PAGE 232

1·12 hydroxystearic acid melting at 83° C. has been isolated from hardened castor oil by *H. Thoms and W. Deckert.*[2]

PAGE 286

For the methods recommended by the Committee of Analysts on standard methods of analysis of seeds, nuts, and kernels, fats and oils and fatty residues, see *Analyst,* 1920, 278 and 286.

PAGE 325

An apparatus designed by *S. H. Blichfeldt and T. Thornley* for determining the melting points under constant conditions is described in *Analyst,* 1921, 180.

PAGE 353

An attempt to identify fatty oils by observing the limits of visibility of the spectra has been made by *H. C. T. Gardner,*[3] whose figures are given below :—

Oil.	Three Inches of Oil Used.		
	Visibility of Spectrum in the Red ends at	Visibility of Spectrum in the Blue ends at	Approximate Extent of Visibility.
	Degrees.	Degrees.	Degrees.
Almond	43	47·3	4·3
Arachis	43·3	45·6	2·3
Castor (East Indian)	Slightly varies about 43·2	45-45·3	2-2·3
Coconut	43·28	47·3	4·02
Colza (2 inches of oil)	43·3	44·6	1·3
Cotton seed (English refined)	43	46·6	3·6
Linseed, Raw	Slight	45	2·0
Linseed, Boiled	43·3	44·3	1·3
Neatsfoot	43·3	45·64	2·34
Olive	Nil	45·3	2·3
Sesamé	43·16	45·6	2·46

PAGE 365

A method and apparatus is described permitting the determination of the absolute viscosity at high pressures.[4]

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[1] *Journ. Amer. Chem. Soc.*, 1921 (43), 938.

[2] *Ber. Deuts. Pharm. Ges.*, 1921 (31), 20.

[3] *Analyst*, 1921, 356.

[4] J. H. Hyde, *Rep. of Lubricants and Lubrication Inquiry Committee*, 1920, 80 and 85.

PAGE 438

L. W. Cook[1] proposes the following formula for calculating the acetyl value from the saponification value of the original oil and of its acetyl product $A(S^1 - S)\ (1 - 0{\cdot}000758)$, where S is the saponification value before and S^1 is the saponification value after acetylation.

PAGE 478

G. Holden and L. Radcliffe[2] have shown that the temperature at which the drying takes place has an important influence on the net increase in weight of the oil. Thus linseed oil dried at 34° C. gained 17 to 18 per cent of its weight; the same oil when dried at 100° C. gained only 7·8 per cent, while at 150° C. no increase in weight took place. This fact has been observed before by *J. Hyland and L. Lloyd.*[3]

PAGE 483

A method of determining the amount of oxygen absorbed during the drying of an oil has been devised by *Krumbhaar,*[4] who distributes over filter paper a weighed quantity of oil mixed with 0·6 per cent of cobalt rosinate. The filter paper is lightly rolled and placed in a U-tube which is kept at 30° C. while a current of dry air is passed through. The volatile products are passed over heated copper oxide and finally through absorption tubes to absorb the water and carbon dioxide. The tubes are weighed every two hours until the weight is constant. A linseed oil treated by this method gained 20·6 per cent in weight after 18 hours. This amount is made up as follows:—0·743 grms. of oil gained 0·128 grms. The amount of hydrogen retained by the calcium chloride tube was 0·009 grms., while the amount of carbon in the soda lime tube was 0·016 grms., making a total of 0·153 grms.

PAGE 485

The following method is recommended by *T. A. Davidson*[5] as giving concordant results in the determination of the ether insoluble brominated glycerides: 4 grms. of oil are dissolved in 35 c.c. of ether (specific gravity 0·717) previously saturated with bromide at 0° C. The solution is cooled to 0° C. and 1 c.c. of bromine added drop by drop from a fine pointed stoppered burette. The tube is then rinsed down with 5 c.c. of ether and allowed to stand at 0° C. for two hours to ensure complete bromination. The tube is then centrifuged for three minutes at 2000 R.P.M. and the liquid decanted. The precipitate is then broken up with a rod and washed with 10 c.c. of chilled ether, cooled and centrifuged as before. This washing is repeated once with ether and finally with 10 c.c. of alcohol (specific gravity 0·820), centrifuging after the alcohol wash at a speed of 1600 R.P.M. Finally the tubes are dried in air until the ether is volatilised, followed by half an hour in the hot-water oven. For the determination of the bromine this observer recommends treatment with sodium ethoxide as described by *Bacon.*[6]

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[1] *Journ. Amer. Chem. Soc.*, 1922 (44), 392. Cp. also E. André, *Comptes rend.*, 1921 (172), 984, and A. Lhys, *Journ. Pharm. Chim.*, 1922 (25), 49.

[2] *Journ. Soc. Dyers and Col.*, 1918 (31), 138.

[3] *Journ. Soc. Chem. Ind.*, 1915, 62.

[4] *Analyst*, 1914, 92. Cp. also S. Coffey, *Journ. Chem. Soc.*, 1921 (119), 1152.

[5] *Journ. Ind. and Eng. Chem.*, 1921, 801.

[6] *Journ. Amer. Chem. Soc.*, 1909, 49.

Page 554

The separation of solid from liquid acids is effected by *Twitchell*[1] by precipitating the solid fatty acids in alcoholic solution by means of lead acetate.

An amount of the fatty acids containing about 1 to 1½ grms. of solid fatty acids is weighed off and dissolved in 95 per cent alcohol; 1½ grms. of lead acetate are also dissolved in 95 per cent alcohol, and the two solutions, which should together amount to 100 c.c., are boiled and mixed. The solution is allowed to stand over night at 15° C., then filtered and washed with 95 per cent alcohol until the washings no longer yield a turbidity on dilution with water. The precipitate on the filter is then rinsed back into the beaker with 100 c.c. of alcohol and 0·5 c.c. of acetic acid, boiled, cooled, filtered, and washed as before. The insoluble lead salts are decomposed, and the fatty acids recovered.

The solid fatty acids prepared by this method have in the absence of iso-oleic and erucic acids iodine values below 1. Cp. also a method by *A. Seidenburg.*[2]

For a method depending on the difference in boiling point between the ethyl esters of the saturated fatty acids and of the brominated esters of the unsaturated fatty acids the original paper by *A. Grun and J. Janko*[3] should be consulted.

Page 590

M. Tsujimoto[4] bases a method for the separation of the more highly unsaturated fatty acids on the solubility of their lithium salts in acetone. His method is carried out as follows:—5 grms. of the fatty acid from which the unsaponifiable matter has been removed are dissolved in anhydrous acetone and neutralised by the addition of an aqueous solution of lithium hydroxide of four times normal strength. The amount of acetone used is made up to 95 c.c., and the water, after allowing for that contained in the alkali solution, to 6 c.c. The solution is cooled in ice for two hours and filtered through a dry filter; 50 c.c. of the filtrate are decomposed with hydrochloric acid and extracted with ether; the ether is distilled off and the acids weighed. The following results have been obtained by this method:—

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[1] *Journ. Ind. and Eng. Chem.*, 1921, 806.

[2] *Journ. Amer. Chem. Soc.*, 1921 (43), 1323.

[3] *Chem. Zeitr.*, 1921 (92), vi. 1239.

[4] *Journ. Soc. Chem. Ind. Tokyo*, 1920, xxiii. 272.

[Table

	Original Fatty Acids.			Highly Unsaturated Fatty Acids.				Acids Freed from Highly Unsaturated Acids.	
	Iodine Value.	Neutralisation Value.	Poly-bromides. Per cent.	Yield. Per cent.	Iodine Value.	Neutral Value.	Refractive Index 20° C.	Iodine Value.	Neutral Value.
Japanese sardine oil No. 1 . .	197	198	...	39·7	369	178	1·4940	75	206
Japanese sardine oil No. 2 . .	194	196	...	40·7	357	180	1·4928	75	205
Japanese sardine oil No. 3 . .	171	187	49	29·9	357	...	1·4965	83	191
Herring oil No. 1	108	193	15	15·0	303	168	1·4890	73	197
Herring oil No. 2	112	192	19	15·3	323	175	1·4900	74	194
Cod liver oil No. 1	169	190	40	29·2	360	172	1·4927	91	196
Cod liver oil No. 2	157	195	...	27·2	343	170	1·4932	88	198
Sun-fish liver oil	164	192	43	30·8	338	174	1·4910	91	194
Whale oil (Balænoptera) . .	114	...	22	16·6	306	177	1·4887	69	196
Whale oil (Megaptera) . . .	119	196	...	15·0	317	179	1·4900	87	197
Whale oil (Rhachianectes) . .	165	197	...	34·9	325	177	1·4890	99	200

PAGE 639

D. M'Nicoll[1] employs for the esterification of the aliphatic acids a 4 per cent solution of naphthalene-β-sulphonic acid in absolute methyl alcohol, which is claimed to ensure more complete esterification than gaseous hydrochloric acid, and also to have no degrading effect on the rosin acids. The method is carried out as follows :—2 grms. of the mixed fatty and rosin acids are weighed off and dissolved in 20 c.c. of a 4 per cent methyl alcoholic solution of naphthalene-β-sulphonic acid. The solution is boiled under a reflex condenser for half an hour, cooled, and titrated with half normal methyl alcoholic potash. A blank of the sulphonic acid solution is treated in the same way, the difference in the two titrations corresponding to the amount of rosin acids present.

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PAGE 27

The presence of minute quantities of petroleum hydrocarbons in extracted oils may be detected by the formolite reaction, as has been shown by *Mashiro Aida.*[2]

PAGE 27

A mathematical study of the general principles of solvent extraction will be found in a paper by *L. F. Hawley.*[3]

PAGE 31

G. Calvert[4] patents a method for converting the free fatty acids in an oil or fat into neutral glycerides.

PAGE 45

Chia seeds (*Salvia hispanica*),[5] a plant indigenous to Mexico, yield on expression 22·33 per cent of oil which had the following characteristics :—

Specific gravity at 15·5° C.	0·9338
Acid value	0·6
Saponification value	192·2
Iodine value	192·2
Unsaponifiable matter	0·8 per cent.

The raw oil resembled perilla oil in its tendency to form drops when spread over a flat surface.

PAGE 82

The influence which the amount of free fatty acids has on the time required for tung oil to solidify in the polymerisation test at 540° F. is shown by the following table, due to *P. E. Jameson*:[6]—

---

[1] *Journ. Soc. Chem. Ind.*, 1921, 124 T.

[2] *Journ. Soc. Chem. Ind.*, 1920, 152 T.

[3] *Journ. Ind. and Eng. Chem.*, 1917, 866.

[4] English patent 143,321, 1919.

[5] H. Gardner and P. Holdt, *Paint Manufacturers Assoc., U.S.A., Circ. 105*, 1920.

[6] *Analyst*, 1920, 328.

Percentage Free Fatty Acids.	Time Required for Polymerisation at 540° F.	
	(*a*) Original Oil.	(*b*) Deacidified Oil.
	Mins.	Mins.
1·9	13	12
2·8	13½	12
4·6	14½	12
4·5	14½	12
2·8	13	11¾
3·7	13½	12
3·8	13½	12
2·4	13	11¾
2·7	13	11½
3·2	13½	11¾
3·3	13	11½
3·4	13½	12

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Lumbang oil is stated by *A. West and Z. Montes*[1] to consist of the glyceride of linolenic acid 6·5 per cent, the glyceride of linolic acid 33·4 per cent, the glyceride of oleic acid 56·9 per cent, and glycerides of solid acids 2·8 per cent. The oil does not polymerise on heating.

PAGE 160

The kernels of the cockle-burr (*Xanthium echinatum*)[2] contained 29·8 per cent of oil; the cold pressed oil was light yellow in colour, with an agreeable taste. The following characteristics were determined :—

Specific gravity at 15·5° C.	0·9251
$n_D^{15·5}$	1·4773
Saponification value	190·2
Iodine value	140·8
Reichert-Meissl value	0·2
Acetyl value	10·6
Melting-point of fatty acids	19·0° C.

The residual cake is stated to have toxic properties.

PAGE 171

A specimen of cantaloup seeds (*Curcumis melo*, L.) examined by *W. Baughman, D. Brauns, and G. Jamieson*[3] yielded 30·4 per cent of an oil having a pale yellow colour and exhibiting the following characteristics :—

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[1] *Philipp. Journ. Sci.*, 1921 (18), 619.
[2] L. B. Rhodes, *Journ. Amer. Chem. Soc.*, 1920 (42), 1507.
[3] *Journ. Amer. Chem. Soc.*, 1920 (42), 2398.

[TABLE

Specific gravity at 25°/25° C.	0·9210
Refractive index at 20° C.	1·4725
Iodine value (*Hanns*)	125·9
Saponification value	192·3
Reichert-Meissl value	0·33
Polenske value	0·26
Acetyl value	15·8
Acid value	0·43
Unsaponifiable matter	1·1 per cent
Insoluble fatty acids	94·0 ,,
Unsaturated fatty acids	80·2 ,,
Saturated fatty acids	14·3 ,,

The oil is stated to be composed of myristin 0·3 per cent, palmitin 10·2 per cent, stearin 4·5 per cent, olein 27·2 per cent, linolin 56·6 per cent.

PAGE 174

The composition of maize oil is stated by *W. Baughman and G. Jamieson*[1] to be oleic acid 45·4 per cent, linolic acid 40·9 per cent, palmitic acid 7·7 per cent, stearic 3·5 per cent, arachidic 0·4 per cent, lignoceric 0·2 per cent, and unsaponifiable matter 1·7 per cent.

PAGE 206

G. Jamieson and W. Baughman[2] give the following composition for cotton-seed oil :—

Myristic acid	0·3 per cent
Palmitic acid	20·0 ,,
Stearic acid	2·0 ,,
Arachidic acid	0·6 ,,
Oleic acid	35·2 ,,
Linolic acid	41·7 ,,

TABLE FACING PAGE 246

The seeds of the hollyhock (*Althœa rosea*)[3] yield a greenish-yellow oil exhibiting a pronounced Halphen reaction, and having a specific gravity at 15·5° C. of 0·9275 and an iodine value of 119·0.

TABLE FACING PAGE 246

The seeds of *Gilletiella congolane*[4] yield to petroleum ether a clear oil which deposits some stearine on standing, and having the following characteristics :—

Specific gravity	0·9159
Saponification value	192·5
Iodine value	93·8
Unsaponifiable matter	1·14 per cent
Free fatty acids	0·79 ,,
Acetyl value	7·0
Melting-point of fatty acids	29° C.
Liquid fatty acids	65 per cent

---

[1] *Journ. Amer. Chem. Soc.*, 1921 (43), 2696.

[2] *Ibid.*, 1920 (42), 1204.

[3] R. Hiltner and L. Feldstein, *Journ. Ind. and Eng. Chem.*, 1921, 635.

[4] A. Boulay, *Bull. Sci. Pharm.*, 1920 (27), 626.

Table facing page 246

The seeds of *Baubinia esculenta*, Burch, known locally as Gemsbok beans, a plant belonging to the leguminosæ, indigenous to South Africa, are described by *G. Bray*[1] as being dark reddish-brown in colour and roughly spherical in shape, measuring about half an inch in diameter. The kernel, which amounted to about 51 per cent of the total seed, was enclosed in a thick woody shell. The kernels yielded 41·6 per cent of a yellow oil having a pleasant taste and exhibiting the following characteristics :—

Specific gravity at 15°/15° C.	0·9211
Acid value	0·6
Saponification value	190·0
Iodine value	95·6
Reichert-Meissl value	0·3
Titration number of the insoluble volatile acids	0·1
Unsaponifiable matter	0·8 per cent
Refractive index $(n)^{40}_{D}$	1·464
Titre	30·6° C.

Table facing page 246

The oil extracted from the seed of the prickly pear has been examined by *S. Lomanitz*,[2] who states that the oil, amounting to 10·89 per cent of the entire seed, was greenish-yellow in colour and had the following characteristics :—

Specific gravity at 15·5°/15·5° C.	0·9294
Refractive index n^{40}_{D}	1·46764
Acid value	3·09
Saponification value	189·5
Iodine value	116·30
Reichert-Meissl value	2·8

Page 252

An account of the botanical nature of Chinese rape seed (*Brassica campestris chinolerfera*) is given in a paper by *A. Vichoever, J. Clevenger, and C. Ewing.*[3]

Page 315

The composition of arachis oil is given by *G. Jamieson, W. Baughman, and D. Brauns*[4] to be as follows :—

	Oleic Acid.	Linolic Acid.	Palmitic Acid.	Stearic Acid.	Arachidic Acid.	Lignoceric Acid.	Unsaponifiable Matter.
Oil from Spanish nuts	52·9	24·7	8·2	6·2	4·0	3·1	0·2
Oil from Virginia nuts	60·6	21·6	6·3	4·9	3·3	2·6	0·3

No hypogaeic acid could be detected.

Page 396

The following figures are recorded for the oil obtained from the seeds of the Concord grape[5] grown in the United States :—

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[1] *Analyst*, 1921, 401.

[2] *Journ. Ind. and Eng. Chem.*, 1920, 1175.

[3] *Journ. Agric. Sci.*, 1920 (20), 117.

[4] *Journ. Amer. Chem. Soc.*, 1921 (43), 1372.

[5] F. Rabak, *Journ. Ind. and Eng. Chem.*, 1921 (13), 1919.

Yield of oil	13 per cent
Specific gravity at 25° C.	0·9204
Solidifying point	−22° to −24° C.
Acid value	0·74
Saponification value	192·2
Iodine value	135·8
Unsaponifiable matter	1·6 per cent

While figures obtained by *E. Andre*[1] for eleven samples of different origins varied within the following limits :—

Specific gravity at 18° C.	0·9103–0·9334
n_D^{18}	1·4708–1·4772
Saponification value	171·0–193·1
Iodine value	94·3–135·0
Acetyl value	13·3–49·3

Table facing page 414

The seeds of *Cynara cardunculus*,[2] the Argentine donkey thistle, yield a deep yellow oil having the following characteristics :—

Specific gravity at 15° C.	0·9213
n_D^{20}	1·4729
Saponification value	197·4
Iodine value	103·5
Solidifying point of fatty acids	29° C.

Table facing page 414

The seeds of *Lindera obstiroba*,[3] known in Korea as "tohaku," yield 60-65 per cent of a brownish oil of which the following characteristics were determined :—

Specific gravity at 15°/4° C.	0·9329
n_D^{20}	1·4653
Solidifying point	−14·4° C.
Saponification value	263·8
Iodine value	70·82
Reichert-Meissl value	2·61
Titration number of the insoluble volatile acids	9·85
Acid value	4·3
Acetyl value	16·42
Unsaponifiable matter	1·60 per cent

The oil yielded 60 per cent of liquid acids and contained capric and a large quantity of lauric acid.

Page 415

The fatty oils obtained from Japanese reptiles have been examined by *Tsujimoto*,[4] whose figures are given below :—

---

[1] *Comptes rend.*, 1921 (172), 1296.

[2] E. Ducloux, *Anal. Soc. Quinn. Argentina*, 1920 (8), 410.

[3] Y. Iwamoto, *Journ. Chem. Ind. Japan*, 1921 (24), 1143.

[4] *Journ. Soc. Chem. Ind. Tokyo*, 1920, vol. xxiii. 273.

	Specific Gravity (15/4° C.)	Acid Value.	Saponification Value.	Iodine Value (Wijs).	Refractive Index (20° C.).	Unsaponifiable Matter. Per cent.	Melting Point of Fatty Acids.	Ether-insoluble Acid Bromides. (Per cent.)	Bromine Content of Bromides. (Per cent.)	Tortelli-Jaffé's Reaction.
1. Leather turtle oil	0·9252	2·0	181·3	128·1	1·4753	7·94	...	37·8	70·66	Bluish green
2. "Akaumigame" oil	0·9249	0·9	192·8	141·4	1·4763	...	...	31·0	70·72	Yellowish green
3. "Ishigame" blubber oil	0·9219	4·1	198·2	103·3	1·4723	...	...	4·6	66·87	...
" liver oil	0·9210	27·1	191·5	114·9	1·4740	...	...	5·4	...	...
4. Viper oil	0·9192	0·4	187·7	110·8	1·4723	1·98	...	7·8	...	...
5. "Yamakagashi" oil	0·9194 (20° C.)	1·1	195·8	102·8	1·4715	1·00	34·5-35·5° C.	11·2	68·03	Bluish green
6. "Aodaishō" oil	0·9139	0·9	194·5	86·5	1·4697	1·22	37° C.	4·7	68·50	Orange yellow
7. Python oil	0·9165 (40° C.)	0·6	194·1	80·3	1·4685 (40° C.)	...	...	2·1	...	Orange yellow
8. Lizard oil	0·9132	21·0	188·8	101·0	1·4647	...	...	9·7	66·16	Brownish-yellow with green nuance
9. "Hikigaeru" oil	0·9348	8·5	181·3	104·4	1·4742	7·94	31-32° C.	1·0	...	...
10. Giant salamander oil	0·9244	1·2	191·2	141·4	1·4765	0·97	...	20·9	67·86	Yellowish green

Page 458

The liver of the prickly dog fish (*Acanthias vulgaris*) yields an almost colourless oil which deposits some stearine on standing. The following numbers due to *T. Lescow*[1] may be reproduced here :—

Specific gravity at 15°/15° C.	0·9125
Acid value	Nil
Saponification value	156·4
Iodine value	110·1
Unsaponifiable matter	12·31 per cent
Glycerol	8·18 ,,
Fatty acids melting-point	27·8° C.
Mean molecular weight	296·1
Unsaponifiable matter melting-point	61·3° to 85° C.
Iodine value	72·9
Melting-point of acetate	Below 100° C.

Table facing page 459

The liver of the tope (*Galeus galeus*), a fish related to the shark family, yields an oil resembling cod liver oil in its characteristics. The following numbers have been recorded by *Chapman*[2] :—

Specific gravity at 15°/15° C.	0·9249
Iodine value	152·2
Saponification value	185·1
Unsaponifiable matter	1·14 per cent.
Refractive index at 15° C.	1·4803
Refractive index at 20° C.	1·4778
Brominated glycerides insoluble in ether	42·5 per cent.

Table facing page 459

The liver of the sea wolf (*Awarrhichas lupus*, L.) yields from 29·6 to 34·5 per cent of a golden-brown oil having the following characteristics[3] :—

Specific gravity at 15°/15° C.	0·9162– 0·9179
n_D^{25}	1·4733– 1·4702
Acid value	13·11 – 14·37
Saponification value	182·8 –185·2
Iodine value	131·2 –118·2
Unsaponifiable matter	5·23 – 3·86
Melting-point of fatty acids	24·5 – 24·7
Mean molecular weight	276·8 –279·9

Page 501

An account of the botanical differences in the species of Chaulmoogra seed and its kin is published in *Bulletin No. 1057*, United States Department of Agriculture, by *Joseph Rock*.

---

[1] *Chem. Umschau*, 1922 (29), 59.

[2] *Analyst*, 1922, 203.

[3] T. Lexow, *Chem. Umschau*, 1921 (28), 213.

Page 624

The kernels of the Curna palm (*Attalea spectabilis*) yielded 65·3 per cent of oil, for which the following characteristics have been recorded[1]:—

Specific gravity at 100°/15° C.	0·8693
Refractive index at 40° C.	1·447
Melting-point	23·6° C.
Solidifying point of fatty acids	24·6° C.
Acid value	1·2
Saponification value	259·5
Iodine value	8·9
Unsaponifiable matter	0·36 per cent
Reichert-Meissl value	6·26
Titration number of insoluble volatile acids	15·6

Page 873

A specimen of the head oil of the sperm whale having the following characteristics has been examined by *M. Tsujimoto*[2]:—

Specific gravity at 15°/4° C.	0·8848
Acid value	0·99
Saponification value	147·1
Iodine value	71·4
Refractive index at 20° C.	1·4633
Reichert-Meissl value	0·57
Unsaponifiable matter	36 per cent
Fatty acids	65 ,,
Glycerol	3·52 ,,
Cholesterol	0·18 ,,

The unsaponifiable matter was resolved into a solid and a liquid portion. The solid portion consisted of cetyl alcohol, while from the liquid portion oleic alcohol $C_{18}H_{36}O$ was isolated. Among the liquid acids physetoleic acid $C_{16}H_{30}O_2$ was identified. This acid on hydrogenation yielded an acid melting at 55°–56° C.

Page 884

The liquid wax secreted by the mutton bird has been examined by *C. Carter*[3] with the following result:—

Specific gravity at 15·5° C.	0·884
Free fatty acids	2·23
Alcohols	38·4 per cent
Saponification value	119·6
Iodine value	130 Wijs 108 Hubl
Viscosity	0·3724

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[1] *Bull. Imp. Inst.*, 1920 (18), 172.
[2] *Journ. Soc. Chem. Ind. Tokyo*, xxiv., 275.
[3] *Journ. Soc. Chem. Ind.*, 1921, 220 T.

Mixed Alcohols

Melting-point	31°–31·5° C.
Saponification value of acetate . .	189

Fatty Acids

Iodine value	150 Hubl 178 Wijs

The alcohols consisted preponderantly of cetyl alcohol.

PAGE 925

A number of Indian beeswaxes examined by *O. Roberts and H. Islip*[1] show the untrustworthiness of the *Weinwurm* test as applied to these waxes.

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[1] *Analyst*, 1922, 246.

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